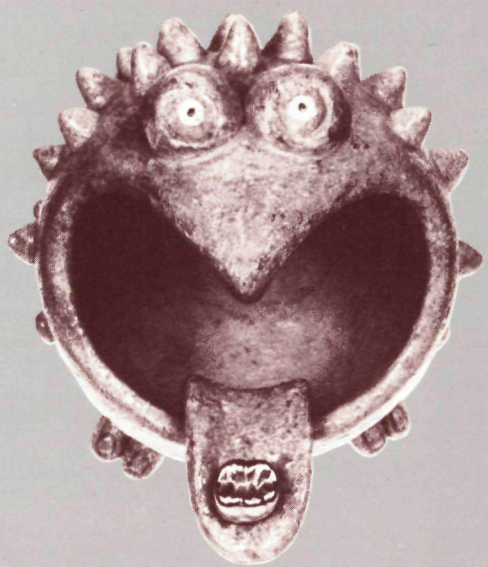
P.R. Mezger



CORROSION BEHAVIOUR OF DENTAL CASTING ALLOYS

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Corrosion taster J Mezger
Photo F L Lourens

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CORROSION BEHAVIOUR OF DENTAL CASTING ALLOYS

SOME PALLADIUM-CONTAINING ALLOY DEVELOPMENTS

Een wetenschappelijke proeve op het gebied van de
geneeskunde en tandheelkunde

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
AAN DE KATHOLIEKE UNIVERSITEIT TE NIJMEGEN
VOLGENS BESLUIT VAN HET COLLEGE VAN DECANEN
IN HET OPENBAAR TE VERDEDIGEN OP
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PETER RICHARD MEZGER
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PROMOTORES:

PROF. DR. A.F. KÄYSER
PROF. E.H. GREENER, NORTHWESTERN UNIVERSITY, CHICAGO
PROF. DR. F.C.M. DRIESSENS

CO-REFERENTEN:

DR. IR. M.M.A. VRIJHOEF
DR. A.L.H. STOLS

From the department of Occlusal Reconstruction (head Prof Dr A F Kayser) and the department of Dental Materials (head Prof Dr F C M Driessens)
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CHAPTER 1

General introduction

Crown and bridgework has been used in many ways since dentistry existed. However, a more critical approach in the application of methods and materials dates back to the first decades of this century. Since around 1930 crown and bridgework is widely accepted in restorative dentistry to rehabilitate mutilated dentitions. Dental materials scientists generally express the alloy's functional qualities in terms of properties characterizing the oral situation as far as physical, mechanical and electrochemical loading is concerned. Clinicians are also concerned about biological acceptability aspects like adverse local soft tissue reactions and deleterious systemic effects.
In this chapter the current state of the art with respect to chemical composition, physical properties, corrosion as well as biologic aspects of corrosion of casting alloys is described. Moreover, the objectives of the study are outlined.

1.1 The evolution of casting alloys

In the 1920s the American Dental Association (ADA) formulated chemical requirements for the traditional type I, II, III and IV alloys. The gold and platinum group metals content should exceed 75, 78, 78 and 83 wt% for type I-IV respectively. Essentially, these traditional systems are Au-Ag-Cu alloys. Within the constraints of the ADA specification's chemical composition, manufacturers have optimized the alloys' properties by means of a proper Cu/Ag-ratio and by adding a certain amount of platinum and palladium. Grain refiners and other dedicated minor components completed the alloy. Mainly for economical reasons, alternatives to the classic type III and IV alloy systems have been developed. Although the Ag-Pd type of alloy already was introduced before World War II, most alternative alloys were developed in the 1970s. Apart from the chemical composition, hardness values were used to classify the traditional systems. Hardness is often utilized to characterize the types of alloy developed recently as alternatives to the conventional ones.
It is obvious that the alternative systems do not satisfy the ADA specification's requirement as to their chemical composition. Therefore, on the basis of the gold content another classification of noble alloys, as proposed by Vrijhoef (1984), will be used in this study (table 1-1).

In the recent past, it has been a general trend to lower the gold content. Both Ag and Cu content reportedly increased, while the Pd content became increasingly

Table 1-1 Alloy classification of alternative noble alloys according to Vrijhoef (1984).

Class	Gold content (wt%)
0: 'no' gold	$0 < Au \leq 20$
1: low gold	$20 < Au \leq 40$
2: medium gold	$40 < Au \leq 60$
3: high gold	$Au > 60$

important to warrant an acceptable tarnish and corrosion resistance. A class 3 alloy (Au > 60 wt%) can hardly be described as a so-called alternative, because its gold content is virtually equal to that of an ADA specification type of system.
The different alternative classes show a considerable overlap in chemical composition (see figs. 1-1 to 1-4).

Porcelain-fused-to-metal (PFM) alloys have been introduced on the market approximately thirty years ago. Since 1958 Au-Pt-Pd alloys have been available. They contain 77-88% Au with considerable additions of Pt and Pd and minor amounts of some other elements. A gold reduced (45-75 wt%) PFM alternative, the Au-Pd-Ag alloy, has been used since about 1970. Virtually no Pt, a large variety in Pd (4-44%) and an increase of Ag up to 16 wt% may be present. At the end of the 1970s, silver free modifications of the Au-Pd-Ag system, the so-called Au-Pd alloys were introduced and gained popularity. The fact that the system was used as a control alloy in a large scale study, started in 1980, on the clinical behaviour of base-metal alloys (Morris, 1986), is evidence that the Au-Pd alloys are considered to be reliable PFM-systems.

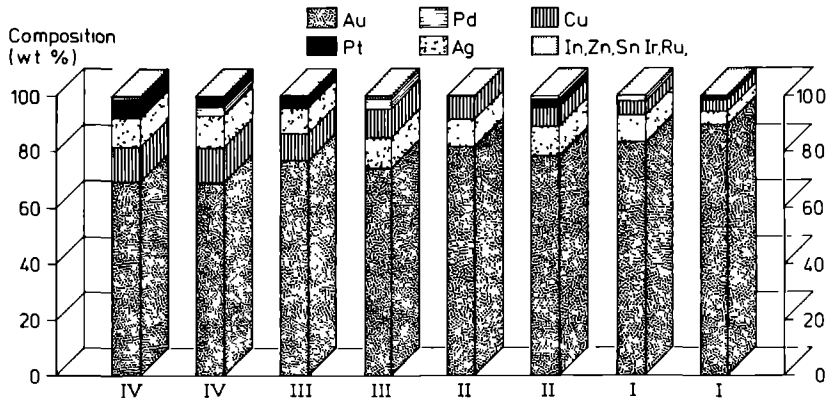

Fig 1-1 Representative examples of the chemical composition of the ADA specification type I-IV alloys (Vrijhoef, 1984).

The fairly new Pd-Ag alloys hardly contain any gold The Pd content varies from 50 to 60 wt%. The amount of silver varies from 24-42 wt%. The most recent development (1981) in Pd-based alloys is formed by the high-Pd alloys They contain about 80 wt% Pd as well as other components, like gallium, copper, cobalt or indium. Fig 1-5 depicts composition limits for the different types of noble PFM-alloys

The majority of the current base metal alloys belong to the nickel-chromium type. They were introduced for use as commercial porcelain-bonding alloys around

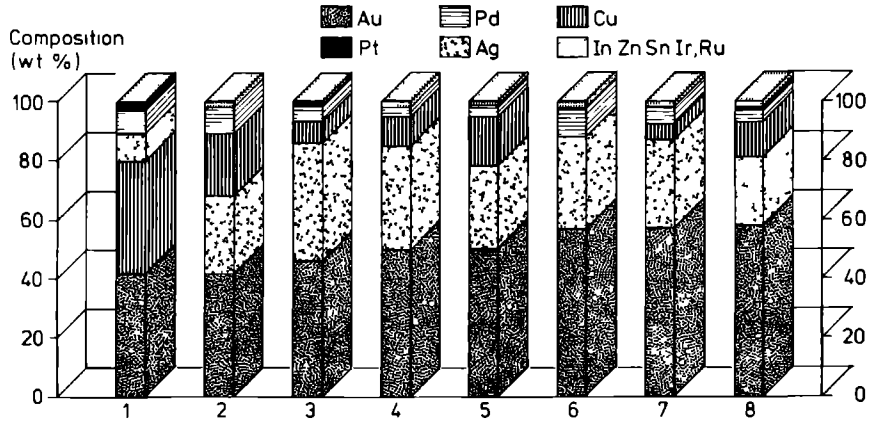

Fig 1-2 Typical chemical compositions of 8 alternative Class 2 (medium-gold) type III/IV casting alloys (Vrijhoef, 1984).

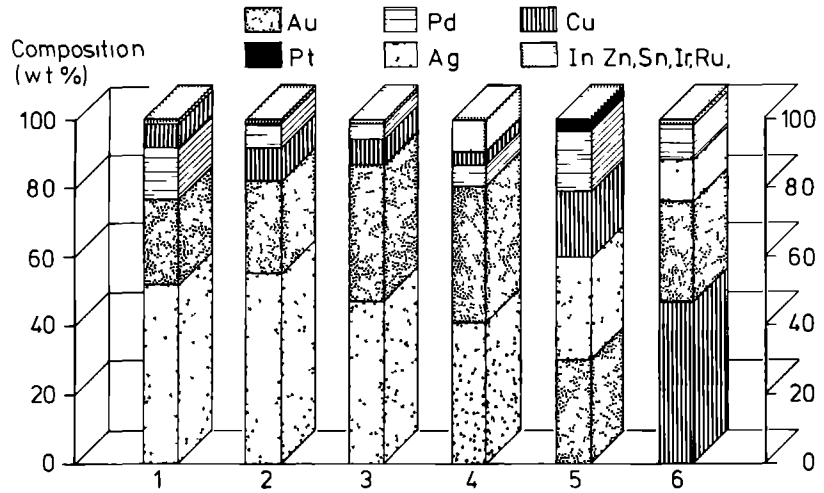

Fig 1-3 Representative chemical composition of 6 alternative Class 1 (low-gold) type III/IV casting alloys (Vrijhoef, 1984).

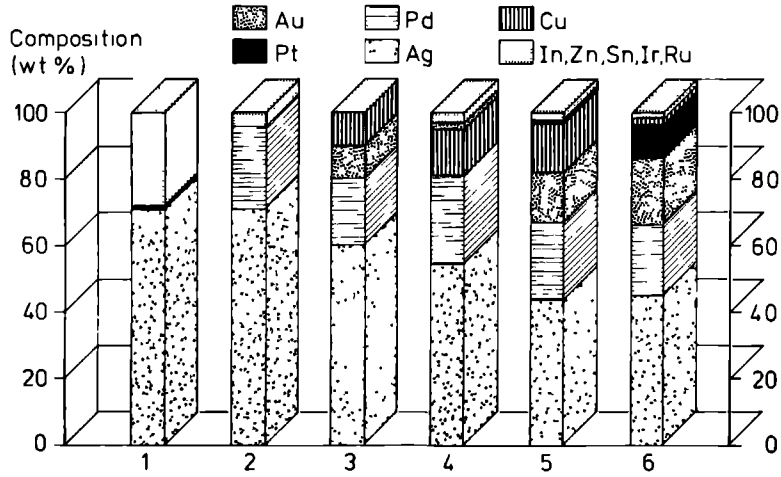

Fig 1-4 Typical chemical composition of 6 alternative Class O ('no' gold) type III/IV casting alloys (Vrijhoef, 1984).

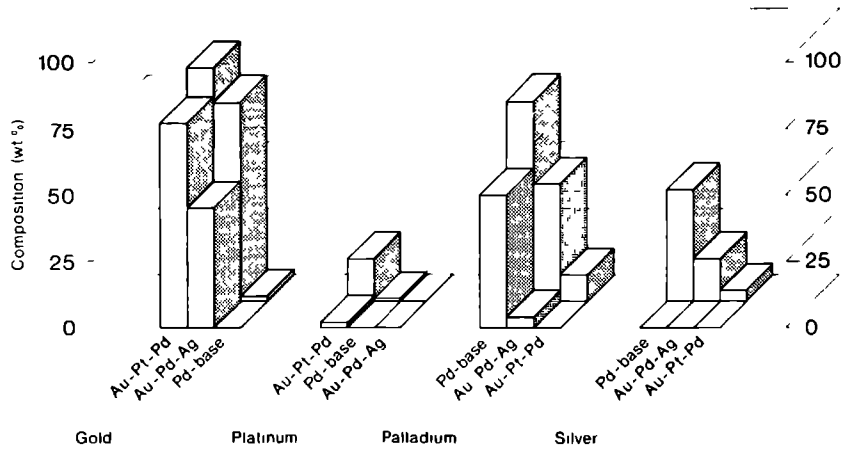

Fig 1-5 Composition limits (minimum in front; maximum in background) for the different types of precious and noble PFM alloys (modified from Vrijhoef, 1982).

1970 (Weber, 1985a). Their nickel content ranges from 60-85 wt%. Chromium content ranges from 5-22 wt% Molybdenum is a third important component. Furthermore, a large variety of balance-elements is used. Beryllium is sometimes added for castability, grain refining and increasing hardness.
Ni-Cr-Be alloys are very popular in the acid-etch bridge realm, because they can be electrochemically etched in a reliable and convenient way.
Ni-Cr alloys have a relatively low density, which is an advantage in certain clinical situations The chemical composition of Ni-Cr PFM alloys is depicted in fig. 1-6.

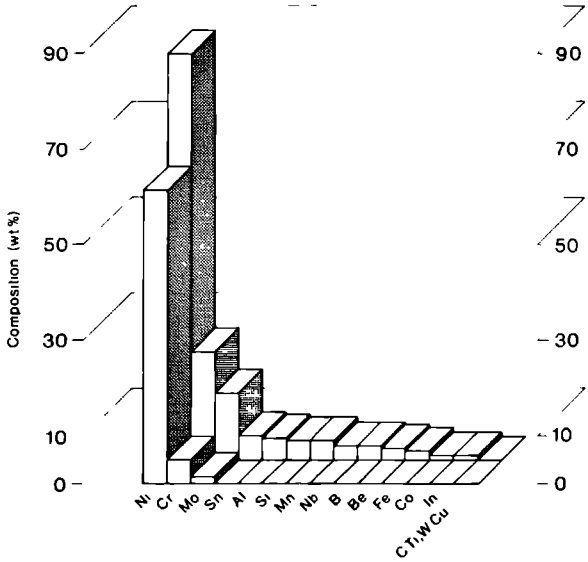

Fig 1-6 Variation of the chemical composition (wt%) of PFM NI-Cr alloys (Vrijhoef, 1982).

Some Co-Cr ceramic alloys, derived from partial denture casting systems, have been introduced in the 1980s. The cobalt content ranges from 52-70 wt%, chromium from 20-32 wt% and molybdenum from 0-10 wt%. As usual a multitude of minor elements may balance the composition. Although some favourable preliminary results have been reported (Siebert, 1983, 1985), at date cobalt-chromium type PFM-alloys are hardly used in dental practice.

1.2 Physical properties

Physical properties are used as a criterion to select a particular casting alloy. It is evident that dental technicians tend to emphasize properties relevant to the handling process in the laboratory. Dentists are also extremely concerned about characteristics which are thought to be of importance to the functioning of the restoration under oral conditions. Both dedicated handling aspects and clinical functioning are of ultimate importance to attain an adequate health care in the restorative field.
A survey of physical properties of the respective alloy types has been given by Vrijhoef (1982, 1984). It is beyond the scope of this study to dwell at length on this subject. However, some trends will be illustrated. Physical properties of high-Pd alloys were hardly investigated at date, so they were not included in the section on PFM alloys and figs. 1-9 and 1-10. Preliminary data on some of these alloys (Mezger et al, 1985a) indicated that their properties are situated well within the range of accepted commercial systems.

Table 1-2 Relevancy of selected characteristics of dental casting alloys and their restorations as to economic laboratory and functional aspects.

Property	Aspects		
	Economical	Technical	Functional
Density	+	+	±
Fit of casting	±	+	+
Young's modulus	−	±	+
Yield strength	−	±	+
Resilience	−	±	+
Burnishability	+	+	±
Solidus/liquidus temperature	+	+	−

+ : obvious relevance
± dubious relevance
− : no relevance

Table 1-2 shows the relevance of some characteristics of alloys and their restorations to economic, technical and functional aspects.
Often there is a condiserable degree of overlap between proprietary traditional systems and their alternatives. The density (fig. 1-7) and the yield strength (fig. 1-8) of type I - IV alloys and their alternatives illustrate such an overlap. However, within each group differences occur.

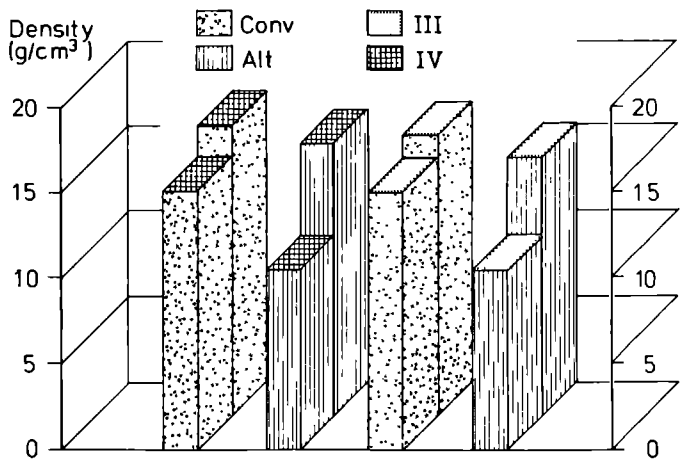

Fig 1-7 Density variations for the respective (alternative) type III/IV casting alloys (Vrijhoef, 1984).

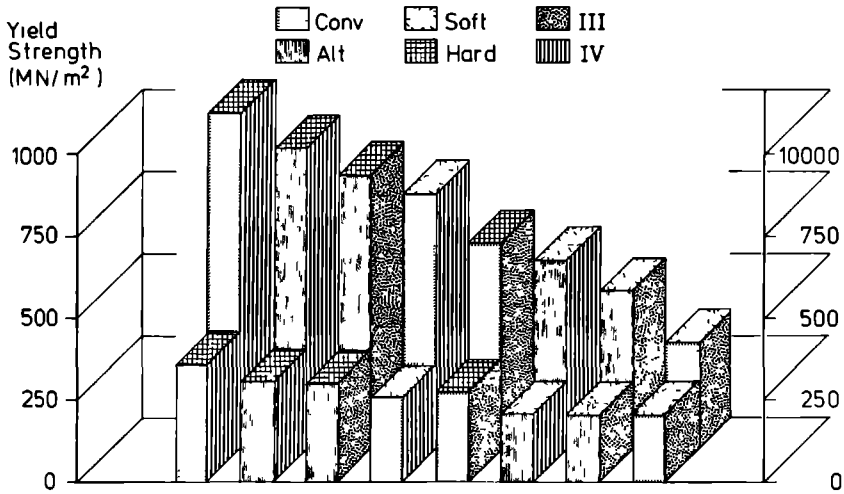

Fig 1-8 Yield strength variations for respective (alternative) type III/IV casting alloys (Vrijhoef, 1984).

The density of the different PFM alloy groups shows virtually no overlap. The range of density values decreases roughly from 16-19 g/cm^3 for Au-Pt-Pd via 12-16 g/cm^3 for Au-Pd-Ag and 11 g/cm^3 for Pd-Ag alloys to about 8 g/cm^3 for Ni-Cr alloys. The density may strongly affect the price of a crown or bridge.
The modulus of elasticity (Young's modulus) is an indication for the stiffness of porcelain-bonding alloys. Stiffness should be sufficient to avoid deleterious stresses in the porcelain From fig 1-9 it is clear that Au-Pt-Pd alloys generally have the lowest modulus of elasticity The lowest values of the Ni-Cr alloys (with or without Be) coincide with the highest of the three other alloy groups Alloys with the lowest

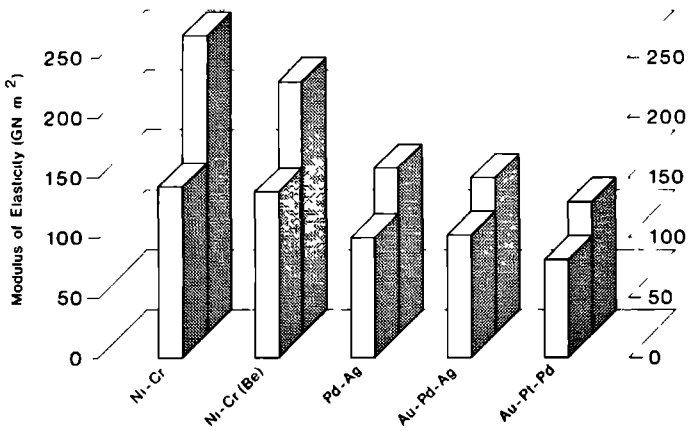

Fig 1-9 Variation of the modulus of elasticity (Young's modulus) for the distinct types of ceramic alloys (Vrijhoef, 1982).

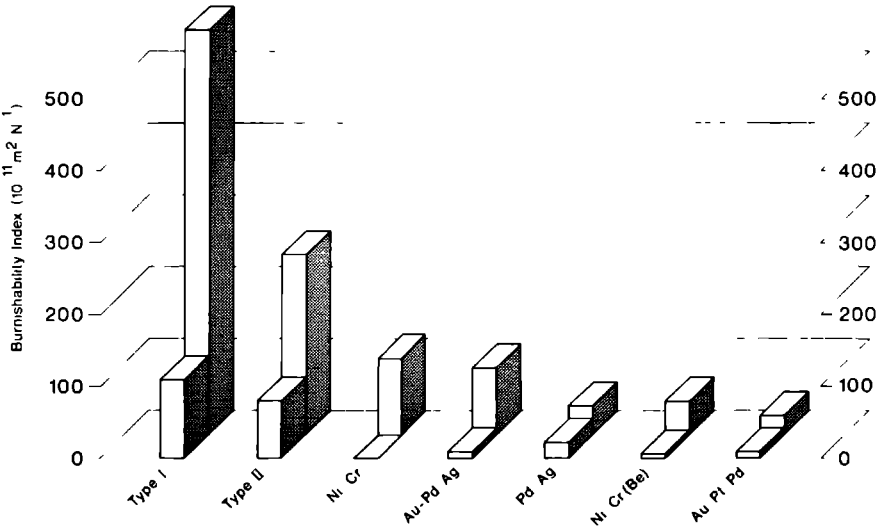

Fig 1-10 Variation of the burnishability index for the respective types of ceramic alloys (Vrijhoef, 1982).

values for the modulus of elasticity in fig. 1-9 may have an insufficient stiffness to sustain a large span bridge. Where rigidity is a prerequisite, a nickel containing base metal alloy with a high modulus of elasticity might be the alloy of choice.
In fig. 1-10 the burnishability index of PFM alloys is defined as the ratio between the elongation and the yield strength. Soft (type I) and medium (type II) ADA specified alloys are included as means of comparison. The type I and II alloys with the lowest values are not burnishable. So, in general, ceramic alloys cannot be burnished at all.
From figures like 1-7 to 1-10 certain tendencies in alloy properties can be found. However, care should be taken not to extrapolate characteristics of a particular alloy blindly. Within each alloy group a range of values for an individual casting alloy is possible.

Because all manufacturers emphasize the casting alloys' physical characteristics, it is possible to make a reasonable selection of a casting alloy as far as these properties are concerned. However, this is not the case for the materials' electrochemical behaviour. This is to be considered as a major shortcoming.

1.3 Corrosion

1.3.1 Tarnish

Tarnish is a surface discoloration on a metal or even a slight loss or alteration of the surface finish or lustre. In the oral cavity it frequently can be correlated to the

formation of hard and soft deposits such as calculus and plaque. Staining arises from pigment-producing bacteria, drugs (containing e.g. iron and mercury) as well as adsorbed food debris. Discoloration on the restoration's surface also might be caused by the formation of thin films, such as oxides, sulphides or chlorides. The nature of such a film may vary from a simple deposit or a protective film to the first step in a corrosion process (Phillips, 1982).

Apparently, it is a combination of several different phenomena and there may or may not be a relation with corrosion. However, it should be stressed here that as a clinically observable phenomenon, tarnish is considered to be of importance to both dentist and patient.

Two investigations on in vivo tarnished crowns clearly illustrate its different aspects. Tucillo and Nielsen (1974) analyzed discolored areas on full veneer crowns with an electron microprobe and found, depending on the type of high-gold alloy, areas enriched in silver sulphide or copper sulphide while sometimes carbon was detected. However, on tarnished crown and bridgework from high-gold alloys, Reppel (1985) could not find any sign of corrosion products. Qualitative analysis of the alloy's surface suggested that the chemical elements found, could all be correlated with components of a normal dietary intake. The morphology of the surface configurations found, was related to deposits of plaque and calculus.

In dental literature, the visual aspect of discoloration has drawn considerable attention. Most research focussed on alloys of the Au-Ag-Cu type and sulphide containing environments. Tucillo and Nielsen (1971) described a rotating wheel tarnishing device, providing both the possibility of submersion and differing aeration of alloy samples. Using a sulphide solution, they found tarnish to favour subsurface porosities and regions of copper deposits (probably due to a contaminated pickling solution).

The relationship between tarnish on the one hand, and alloy composition and microstructure on the other, has been investigated (Ingersoll, 1975; German *et al.*, 1982; Herø and Jørgensen, 1983; Herø and Valderhaug, 1985; Corso *et al.*, 1985). Hultquist and Herø (1984) pointed out that Cu (in contrast to Ag) in dilute solutions of sulphide and chloride selectively dissolved from single phase gold-based alloys, without subsequent precipitation or staining corrosion products. Both in a chloride containing artificial saliva and a sulphide solution, the silver-rich regions in a gold-based alloy were subject to tarnishing (Corso *et al.*, 1985). Pd-alloying was found to reduce the tendency to sulphide tarnishing (Vaidyanathan *et al.*, 1979; Lang *et al.*, 1982; Suominen *et al.*, 1985).

The tarnish behaviour of Ag-Pd-Cu alloys was extensively investigated both in vitro and in vivo (Niemi and Holland, 1984; Niemi and Herø, 1985; Herø and Niemi, 1986). In this type of alloy, tarnish only occurred in silver-rich areas. Again, the increase of palladium content enhanced the tarnish resistance.

To quantify discoloration due to tarnish, Burse *et al.* (1972) and Ingersoll (1975) devised ordinal scales for direct visual use. Lubovich *et al.* (1979), German *et al.* (1982) and Marx and Stender (1984) used light reflectivity on different alloy surfaces. Obviously, it is a problem to create stable testing conditions. Marx and

(1984) pointed at filter choice problems of the spectrophotometer and the difficulty to reach a consistent base-line alloy surface polish. Moreover, Chana and Kuhn (1984) indicated the lack of stability of the sulphide solution used in tarnish testing.
In general, the tendency to perform tarnish tests in sulphide containing environments has been stressed. German *et al.*, (1982) indicated that also chloride and phosphate environments should be considered, especially for Pd-base alloys. Sutow *et al.* (1979) showed that also base metal alloys are not sulphide tarnish prone. Consequently, with the large variety of new developments in ceramic alloys, a number of tarnishing electrolytes, specific for each alloy group, should be used.
A strong patient depending effect is noticed in clinical tarnish behaviour (Burse *et al.*, 1972; Letzel *et al.*, 1983). Also methodological problems do occur in evaluation of clinical tarnish (Mezger *et al.*, 1985b).
Summarizing it might be stated that tarnish is a combination of different phenomena, manifesting itself as discoloration. The phenomenon as such is poorly defined and consequently not a proper parameter to measure (in vitro) corrosion processes. This is all the more evident because testing solutions are related to specific alloy types, so a comparison between groups is impossible. The fact that tarnish is noticed by the dentist as well as the patient, warrants ample attention on the part of the alloy manufacturer. With sufficient attention to the alloy aspect, tarnish is reduced to a mainly patient related problem.

1.3.2 The corrosion process

Corrosion may be defined as a chemical or electrochemical reaction between a material and its environment (ASTM designation G15-85A). It results in pertinent changes of the material's chemical composition and microstructure and thereby may cause unacceptable deterioration of the material as far as its functional properties are concerned. Corrosion results in dissolution of metal ions or in their involvement in the formation of compounds such as oxides and sulphides. Frequently, the initial stages of chemical deterioration of an alloy are heralded or evidenced by tarnish (German *et al.*, 1982).
To define a basis for the corrosion measurements in this thesis, the corrosive process should be briefly introduced. In the moist oral environment, dentistry is mainly concerned with electrochemical or 'wet' corrosion.
A metal put in an aqueous solution has a tendency to dissolve and release ions. Thus a separation of electrical charge occurs. The metal has a net negative charge and adjacent to it, the aqueous solution a positive one. Such a system is called an electrode (West, 1970). The potential established by the metal with respect to the solution cannot be directly measured. However, one can measure a potential difference with another electrode with a potential that is invariant by definition: the hydrogen electrode. Under standard conditions of temperature and acidity and a hydrogen pressure of one atmosphere, the measured potential at which the pure

metal is in equilibrium with its metal ion at unit activity is the standard potential of that metal compared to the hydrogen electrode. Comparing the metals in this way the standard electrochemical or electromotive force series (EMF) can be derived. Metals with large positive potentials are called 'noble' because they do not readily dissolve. More reactive systems are called 'base' metals.
Based on the relative position in the electrochemical series, it is possible to predict whether a metal in a system will spontaneously dissolve. However, the EMF-series suffers from drawbacks. It requires equilibrium conditions, does not apply to alloys and no passivation effects are taken into consideration. To determine the rate of corrosion, information is needed about the kinetics of the electrode processes. Normally, the standard conditions are not realistic, so additional information is required. Immersion of metals in sea water (as a zero order substitute for extracellular tissue fluïd) gives potentials which are somewhat different than those of the standard EMF-series, particularly for metals forming coherent surface films. The resulting ranking order is an example of a galvanic series. For practical reasons the hydrogen reference electrode is often replaced by the saturated calomel electrode (SCE) with a potential of + 0.242 V at 25°C compared to the former one.

Metallic corrosion is controlled by thermodynamic and kinetic factors. Thermodynamic factors decide whether it is energetically possible for a reaction to occur spontaneously. However, kinetic factors determine at which rate the reaction effectively occurs (Scully, 1981).
Pourbaix (1963) measured, collected and calculated thermodynamic data on reactions between metals and water. Combination with solubility data on oxides and hydroxides as well as with equilibrium constants of these reactions resulted in the so-called Pourbaix diagrams: Isothermal phase diagrams which indicate metal-ion-oxide equilibria as a function of electrode potential and pH. In a simplified representation of the diagram (fig. 1-11) areas of immunity (= region of thermodynamic stability of a metal), corrosion and passivity (= region where the stable form is a particular oxide, which may be protective or not) are indicated.

It should be stressed again that Pourbaix diagrams provide a thermodynamic basis for the understanding of corrosion processes. However, kinetic factors are not taken into consideration: it is known that the reaction is going to take place, but its rate is not determined yet. The regions in the potential-pH diagram that are marked in the figure as corrosion, immunity and passivation represent areas where a reaction can, cannot and does not occur under equilibrium conditions (Scully, 1981). Quantification of the rate of a reaction on the basis of Pourbaix diagrams is impossible. Moreover, the known reactions between metal and pure water do not show an absolute predictive value for corrosion phenomena in solutions containing aggressive components e.g. chloride ions.

Electrochemical corrosion is based upon mechanisms which form an electrolytic cell. It consists of an electrolyte, an area of metal oxidation (anode), an area of electron consumption i.e. reduction (cathode) and an external circuit for electron transport.

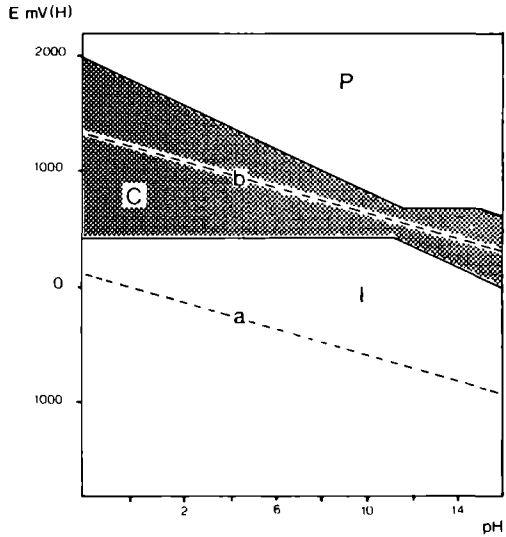

Fig 1-11 Simplified Pourbaix diagram indicating the theoretical domains of corrosion (C), immunity (I) and passivation (P) of silver at 25 °C. The area of stability of water is delineated by a and b.

Several electrochemical corrosion mechanisms play a role in the oral cavity. In case of contact between dissimilar metal restorations, electrogalvanic corrosion may occur. With and without direct contact electrical circuits are built involving saliva as primary electrolyte, the dissimilar alloys as electrodes and the soft and hard tissue and their fluids acting as an external circuit.
Due to its heterogeneity (segregation; multiphase character; impurities), one metallic restoration may constitute numerous anodic and cathodic sites.
Because of their higher free energy, grain boundaries are less stable than the inner sites of grains. This may be the driving force to create stress corrosion at grain boundaries sites. Surface irregularities and pits may act similarly.
In a homogeneous alloy, concentration cell corrosion is possible, providing a local variation of electrolyte occurs. The presence of plaque may create areas with different oxygen concentrations and pH. Local pits covered with plaque will be oxygen depleted compared to their immediate environment. The bottom of the pit will act as a small anode, surrounded by a large cathode, thus promoting rapid corrosion. A survey by Galvele (1983) showed that the pH in a pit at the metal's surface may drop to an extremely low value (< 3) irrespective of the pH of the surrounding electrolyte.

Corrosion is the result of a complicated interaction process between the factors alloy and environment. It is evident that saliva plays a key role in this interaction process. Therefore, important features of the oral habitat will be discussed briefly. The functions of saliva concern digestion, moistening and facilitating swallowing,

protection of mucosa and teeth, regulation of the water balance and buffering of the pH. Consequently, it is a complex system. Saliva is secreted by three large paired glands (parotis, submandibular and sublingual) and many smaller glands in the oral mucosa. For each gland, the secretion varies in composition and quantity depending on various conditions and stimuli. Furthermore, the composition varies from patient to patient. It is therefore impossible to give a distinct quantitative account of saliva composition. Generally, it might be stated that it consists of inorganic ions, small organic molecules and proteins dissolved in water. Saliva may also contain small amounts of fluid from the gingival pocket (crevicular fluid). Due to its mucin content, saliva is a viscous solution. Mucins are glycoproteins of high molecular weight which contain more than 50% carbohydrates (Tabak *et al.*, 1982) Mucins have a certain buffering capacity (i.e. the power to resist changes in pH). Bicarbonate and phosphate buffers are the most important systems involved in saliva (Lilienthal, 1955). Its pH varies with the flow rate.

Dental plaque forms a complex microbial ecological system on the tooth surface and is embedded in a matrix of polymers of bacterial and salivary origin (Marsh, 1980). The composition of plaque varies from one place in the mouth to the other, depending on thickness and duration of presence in situ. The oxygen tension in the inner plaque region is relatively low compared to the surrounding oral region. The pH in plaque may differ considerably from that of saliva (pH = 6.75) if sugar is a component of saliva. Due to bacterial action, saliva may reach values as low as pH = 5 or lower (Jenkins, 1978).

Corrosion studies of dental casting alloys are hindered by a limited knowledge of the oral environment. Critical features of a corrosive environment include pH, redox potential (E_h) of the electrolytic solution and the partial pressure of oxygen and hydrogen. At selected sites on the tongue and the buccal folds, the oxygen concentration shows considerable differences between the distinct areas (Eskow and Loesche, 1971). Furthermore, an oxygen concentration gradient exists between the gingival sulcus covered with plaque and a clean supragingival tooth surface. Likewise, pH values found in deep plaque layers may be lower than elsewhere in the oral cavity.

Marek and Topfl (1986) stated that reliable data on the aggressiveness of the in vivo environment are absent and that its high variability cannot be duplicated in the laboratory.
Palaghias (1985) investigated the influence of a number of separate components of saliva and the role of some selected types of bacteria on the corrosion of amalgam. The carbonic acid-bicarbonate buffer turned out to act as a cathodic inhibitor. The inhibiting effect of the phosphate buffer depends on concentration. In low concentrations the phosphate ion is corrosive.
For some metals used in dentistry, corrosion processes may be affected by organic components in solution (Svare *et al.*, 1970; Finkelstein and Greener, 1978; Clark and Williams, 1982; Mueller, 1983, 1985). Corrosion inhibition by organic

saliva components might occur by means of adsorption on a metallic surface. The adsorbed layer subsequently functions as a diffusion barrier. The stability of such a film is relatively high (Baier and Glantz, 1978), but its chemical characteristics may be altered by a drop in pH (Glantz, 1980).
Stable organic compounds often retard hydrogen evolution more effectively than oxygen reduction (Antropov, 1967). This might explain for the lower current densities observed in the in vitro tests in a deoxygenated environment (Palaghias and Söremark, 1984). Bacteria influence oral corrosion processes through their corrosive metabolic products, the formation of sites of differential aeration and concentration cells. Furthermore, they influence the depolarization of cathodic processes, the disruption of protective films and the breakdown of corrosion inhibitors (Menzies, 1971).

Halogen ions (markedly chloride) are considered to be extremely aggressive components in corrosion. In the presence of aggressive anions, passivity of an alloy or metal cannot be easily established nor maintained. As the concentration of e.g. Cl^- ions is increased, the critical current density (I_{crit}) and the primary passive potential (E_{pp}), both indicators of an onset of passivity, are raised. Also the current density in the passive region is enlarged while the passive potential range becomes smaller. This is probably due to the high charge density on the chloride ion and its easy migration. In the passive potential region, it competes with the oxidizing species and becomes incorporated into the (passive) film. This produces lattice defects, thereby reducing the resistivity of the oxide (Scully, 1981). The chloride ion is also important in the occurrence of pitting corrosion. This type of attack is confined to small areas, while other parts of the metal surface remain passive. For the pitting potential value (E_p), a relationship can be found: $Ep = A\text{-}B \log (Cl^-)$, in which A and B are constants (Galvele, 1983). The importance of halogen ions is reflected in the electrolytes used in laboratory corrosion testing. Saliva substitutes range from simple saline to a number of very complex solutions, where both attack and inhibition activities are simulated.
Meyer and Nally (1975a,b) compared corrosive action both in pooled stimulated saliva and in several saliva substitutes. They reported that a modification of the artificial saliva proposed by Fusayama *et al.* (1963) did correlate best to the corrosion activities of the pooled saliva. This modified artificial saliva was chosen as an electrolyte in our in vitro corrosion study. Furthermore, a simple 0.9% saline solution was used. It represents an approximation of the Cl^- content of biological extracellular fluids and lacks inhibitive components of saliva. Thus it creates an aggressive environment.

Baas-Becking *et al.* (1960), described the limits of 'all' natural environments for geological purposes in terms of pH and oxidation-reduction potential. Thinking along these lines and comparing to earlier work of Eisenbrandt (1945) and Kenney and Ash (1969), Ewers and Greener (1985) developed an envelope of potential and pH values for the oral cavity. For a limited number of subjects with clean and decay-free mouths, they measured at 5 standard sites as well as in pockets

> 4 mm. The subjects were requested not to eat during a 4 hour period previous to testing. Their dental history ranged from minimal previous treatment to past periodontal treatment and extensive crown and bridgework. pH values were found to range from 6.1 to 7.9. The oxidation potential ranged from −58 to +212 mV (SCE). The most reducing potentials were found in pockets exceeding 4 mm depth. Keeping in mind that the values found in this study concerned clean, decay-free mouths, and a combination with an anodic boundary value of an area of interest suggested by Corso *et al.* (1985), leads to a tentative zone for corrosion tests of −100 mV to +300 mV (SCE). This zone will be indicated as the 'area of oral interest'.

1.3.3 Biological aspects of corrosion

Cast restorations are used in dentistry as a means to remedy impaired function and esthetics of the dentition. Corrosion in the oral environment may pose certain biological and mechanical problems resulting in a reduced longevity of the restoration. As indicated before, metal ion release occurs in the oral cavity. Knowledge about the release of various elements from dental alloys with respect to concentrations and chemical state is essential to evaluate possible local or systemic biological effects. However, information about the release of specific elements in natural or artificial saliva under in vitro or in vivo conditions turns out to be scarce (Brune, 1986). The number of components used in dental casting alloys is large. The variations on a certain alloy theme seem to be virtually unlimited. Consequently, detailed research about characteristics relevant to biological aspects will be extremely time consuming and virtually impossible. Questions about dietary intake and essentiality to human metabolism are only partly solved (Underwood, 1971; Friberg *et al.*, 1979; Jacobsen *et al.*, 1981; Curzon, 1983) and subject to continuous research. Up to now, crown and bridge alloys do not seem to pose major problems. Trial and error and clinical experience have eliminated grossly corroding dental alloy systems. Even though gross corrosion is not seen, a substantial cation flux may occur. For a metal with a corrosion current density of 0.1 $\mu A/cm^2$, releasing monovalent ions, this flux could be $0.6x10^{12}$ ions per cm^2 per second. For more complex alloys, showing a release of different types of ions, the release ratio and valency of respective ions are important. The cation flux will probably not result in mechanical failure, but depending on the quality of ions released and the interaction with the direct environment, it may burden the biological system. Precise acceptable levels satisfying the fundamental requirements of safety and health are unknown.
In the limiting confines of the introduction to this study we are concerned with the adverse effects of ions possibly released from metallic dental restorations and their eventual reaction products in the human body.
Noxious effects (toxic and carcinogenic) from metal dust and vapors of elements such as nickel, chromium and beryllium in industry are documented (Moffa, 1973; Kristiansand Conference, 1978; Friberg *et al.*, 1979). Risks to dental techni-

cians are described (Moffa, 1973; Davidson, 1982; Brune and Beltesbrekke, 1983; Klötzer, 1985). Noxious effects to patients due to metal sensitivity from dental castings are known from case reports (Levantine, 1974; Fisher, 1974; Bork, 1978; Fregert, 1979; Tilsley and Rotstein, 1980; van Loon, 1982; Hartmann, 1984; Kalkwarf, 1984; Gasser, 1985). Often base metals are thought to be related to adverse effects. However, a case of Pd sensitivity from a conventional Au-Pt-Pd bridge has also been reported (van Loon, 1982). And even the gold component in high-gold alloys reportedly may bring about allergic reactions (Fregert *et al.*, 1979; Holland-Moritz *et al.*, 1980; Hermann, 1981; Shepard *et al.*, 1983; Wiesenfeld *et al.*, 1984). In a literature search, Hermann (1985) counted 20 case reports of allergic contact reactions related to high-gold alloys in the mouth. He concluded that current dental alloys seldom lead to allergies but apparently gold alloys are most often involved in reports.

One case history on a squamous cell carcinoma on the tongue, physically related to a 'metallurgically flawed' gold alloy crown, 15 years in situ, could be found in literature (Kinnebrew *et al.*, 1984).

Since a long time, the galvanic action of dissimilar alloys and related (oral) biological implications get ample attention in literature. Clinical manifestations of oral galvanism, including casting alloys, have been described in case reports (e.g. Mumford, 1960; Inovay and Banoczy, 1961; Carter, 1965; Perko, 1967; Bales and Mahew, 1982; Rossa, 1984). Oral symptoms described, include metallic or battery taste, burning, smarting of itching of the tongue, cheeks and lips and increased or decreased salivation. Symptoms are much more pronounced when the physical and/or the mental condition is weakened or when hormonal changes occur (menopause), when the oral hygiene is neglected and when acid foods or certain drugs are used (Glick *et al.*, 1976; Söremark, 1979). Also a link with the prevalence of oral lichen planus or leukoplakia has been put forward (Inovay and Bánóczy, 1961; Bánóczy and Sugár, 1972; Kövesi and Bánóczy, 1973; Bánóczy, 1977; Bánóczy *et al.*, 1979). A low secretion rate of unstimulated saliva and a low pH and buffer capacity often is found in patients with oral lichen planus (Lundström, 1984). According to Palaghias (1985), this could imply an impaired protection against clinical corrosion, as he showed that the inhibiting effect of the phosphate salivary buffer system was concentration and pH dependent. This might explain the increased incidence of allergy for e.g. mercury in the oral lichen planus groups as found by Finne *et al.* (1982) and Lundström (1984). Syrjänen *et al.* (1985a) reported mucosal changes near combinations of different metallic restorations. However, for all these manifestations cause-effect relationships have not been established.

Schriever and Diamond (1952) have reviewed the early literature on electrogalvanic action. Like Mumford (1957), they indicated a number of possible current paths related to the oral galvanic action of dissimilar alloys. Soft and hard oral tissues with their respective fluids and saliva as primary oral electrolyte, could close such electrical circuits. Numerous authors have attempted to quantify electrical aspects of galvanic action including dental casting alloys in vitro (e.g. Fusayama *et al.*, 1963; Marxkors, 1965; Maschinsky, 1970; Fraunhofer and Staheli, 1972;

Gjerdet, 1980; Holland, 1980; Zitter and Pitner, 1983; Griffin *et al.*, 1983; Arvidson and Johannson, 1985; Momoi *et al.*, 1986).
Research concentrated on methods and measurements for evaluation of oral electrochemical action. Therefore, the potential of a restoration versus a reference electrode, potential differences between distinct restorations and direct or indirect recording of currents have been reported (see e.g. table 1-3).

Table 1-3 Some examples of in vivo measurements related to electro galvanism according to author.

Author(s)		Measurement
Schriever and Diamond	(1952)	E
Mumford	(1957)	E
Köhler	(1958)	E
Inovay and Banoczy	(1961)	E
Chiru-Mocanu *et al.*	(1969)	E
Laudenbach and Recoing	(1969)	E
Maschinski	(1970)	E
Wagner and Till	(1972)	E, R
Lukas	(1973)	R
Gjerdet and Brune	(1977)	E, I_{ind}
Bergman *et al.*	(1978)	E, I_{ind}
Nomoto *et al.*	(1979)	E
Lukas	(1981)	I
Nilner	(1981)	E, I_{ind}
Bergman *et al.*	(1982)	E, I_{ind}
Lundmark *et al.*	(1982)	E, I_{ind}
Axell *et al.*	(1983)	E, I_{ind}
Johansson *et al.*	(1984)	E, I_{ind}
Yontchev *et al.*	(1986)	E
Johansson	(1986)	I

E : potential difference
I : current
R : resistance
I_{ind} : indirectly calculated current

Early measurements aimed at potential (difference) registration. As charge transfer is the basis of ion release in a circuit, this is not a proper approach. Later on, methods to measure in vivo galvanic currents were developed.
One major problem related to all of these tests is of fundamental importance. Measurements on the resistance of any type of oral tissue have not been presen-

ted (Nilner, 1981). The relevance of the methods to measure galvanic currents between restorations in vivo is therefore still open for discussion. So far no relation has been established between the different measurements and distinct patterns of complaints.
A short survey on the different comprehensive studies in the Scandinavian countries with respect to oral galvanism may elucidate this. In a comparative study of patients with oral discomfort of a possible galvanic nature and a control group, Nilner (1981) could not find any significant differences in galvanic currents or ions released.A higher amount of restorative care at a comparatively lower level of technical quality was noticed in the patient group, along with a lower threshold level for metallic taste perception. These findings were confirmed by Axell *et al.* (1983). Moreover, a great need for treatment of mandibular dysfunction was seen in the patient group. Jontell *et al.* (1985) found no differences between alleged oral galvanism patients and a control group, except for the amount of parafunctional activities. Patients in the test groups gave evidence of 'being more exposed to negative social events' and the results indicated a psychogenic component behind the reported complaints. Johansson *et al.* (1984) and Agerberg (1987) related signs of advanced periodontitis with the occurrence of intra-oral burning and smarting sensations. Unlike Nilner (1981) and Axell *et al.* (1983), Johansson (1986) did not find any differences in metallic taste perception. However, she found a relatively large number of periodontal and mucous membrane affections, carious lesions and stomatognatic and/or temporomandibular joint disturbances within the patient group. In a group of patients with orofacial discomfort, Yontchev (1986) could not find a single cause for the complaints, such as 'oral galvanism' or 'metal syndrome', but a very heterogeneous etiological background instead. He stressed that especially in Sweden, oral galvanism is a 'mass media phenomenon'.

Much effort is put into the increase of knowledge on biological aspects of metals and alloys related to dentistry. The use of cell culture tests (Kawata et al., 1981; Niemi and Hengsten-Pettersen, 1985; Arvidson *et al.*, 1986; Rae, 1986), animal tests on various aspects of allergy and toxicology (Bergman *et al.*, 1980; Vreeburg *et al.*, 1984; Syrjänen *et al.*, 1985b), tongue scraping and saliva sampling to detect amounts of metal release (Stenberg, 1982; De Melo *et al.*, 1983) or the relation between mucosal and dermal sensitivity to allergens in man (Nielsen and Klaschka, 1971; Van Loon *et al.*, 1984) are currently reported. Also efforts are made to relate quantities of alloy consituents released from restorations to food and drink intake of these elements (Weber, 1985b; Brune, 1986). However, their ultimate biological relevance is hard to establish while the amount of conflicting data is overwhelming.
Up to now, an internationally accepted uniform protocol for biocompatability testing is lacking (Mjör *et al.*, 1985).
The enormous amount of new or constantly slightly changing old alloys, marketed by dental manufacturers, further complicate testing procedures and prevent an intelligible use of alloys in dentistry.

1.4 Objectives of the present study

The prime objective of this study is to increase the knowledge about the corrosion behaviour of dental casting alloys used for crown and bridgework.
Many aspects of oral corrosion are unknown. It is a complex process influenced by several environmental factors. Existing studies on this subject are very diverse and often not comparable. To improve this situation the following aims are formulated:

- To create an in vitro corrosion data base comprising the current accepted alloy spectrum, using established electrochemical techniques.
- To investigate the influence of mucin in a commercial saliva substitute for xerostomic patients on the in vitro corrosion behaviour of some dental casting alloys.
- To place three types of palladium containing recent alloy developments on the corrosion map.
- To investigate and subsequently relate metallurgical aspects of the recent Pd containing alloys with their in vitro corrosion behaviour.
- To relate the results of a short-term clinical trial using cast restorations of different alloy types in one mouth, with the in vitro corrosion behaviour.
- To assess the predictive value of a short-term clinical trial for a long-term restoration type.

Corrosion is a process promoting degradation of metallic restorations with possible mechanical and biological consequences. An ordering of the casting alloy spectrum, according to corrosion behaviour and chemical composition, is relevant on biological and economical grounds. Results of this study may add to facilitate the dentist to select alloys based on scientific facts.

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CHAPTER 2

2 Corrosion of current market alloys

In chapter 1 it was shown that many different corrosion mechanisms may play a role under oral conditions. These phenomena are influenced by a multitude of environmental factors. It is obvious that in defining a laboratory test, a selection should be made from the numerous mechanism/factor combinations. Indeed, in literature many different tests can be found, making it extremely difficult to genuinely compare one investigation to another one. Generally only a few alloys are studied, so it is virtually impossible to locate a particular system in the alloy spectrum as a whole. Therefore, it is the aim of this chapter to create the armamentarium to which systems investigated in the chapters 4 to 6 can be compared.

2.1 Selection of the alloys investigated

An overwhelming number of commercial dental casting alloys is available. The introduction of new systems appears to be a continuous process. Dental laboratories seem to have interest to be supplied by one manufacturer. Therefore, most manufacturers produce the whole spectrum of alloys, representing the current state of dental casting art. Because many alloys are a variation on an older theme, considerable overlap is to be expected between the gamuts of different competing systems.

Accurate information on dental casting alloy composition is not easily obtained. Manufacturers tend to be rather secretive about this subject for reasons of competition. An alloy may be patent protected, but variations on the patent description are easily found and therefore numerous substitutes in a particular system can be made available.

On the one hand, compositional changes may occur to improve its characteristics or for patent-related purposes (many a time this occurs without a change in brand name). On the other hand, insignificant variations of chemical composition may lead to 'new' and 'improved' alloys. In this case, of course, new brand names will be advertized.

In dental literature sometimes surveys on the chemical composition of dental casting alloys are published, based on manufacturers data (NMT, 1984; ADA, 1984; FZV, 1986). Frequently, the information offered does not include more than 90 wt% of the total composition. Brochures for dental technicians may even be less informative. For instance, an alloy composition may be described as containing 80 wt% noble metal (Au + Pd) for an alloy actually containing 79 wt% Pd and 1% Au, while a description of the residual 20 wt% is omitted completely.

The dental technician and the dentist have a special relationship based on a

mutual dependency. The dental technician should provide adequate work based on a detailed demand from the dentist. When dental laboratories change from one alloy supplier to another one, this change is not always notified to the client-dentist. From his part, the dentist may only ask for a particular type of alloy rather than for a specific brand name or chemical composition. In both cases, alloy information will be at least incomplete. It has been advocated by Vrijhoef (1984) to include the brand name and alloy composition in the patients file. From the previous it is evident, that a dentist can hardly take responsibility for his own patient files as far as casting alloys are concerned.

To select the alloys used in this study, manufacturers' data formed a starting point. Then a survey was made of the different alloys used by 30 Dutch dental laboratories of various sizes from all parts of the Netherlands. Twenty laboratories were asked to cast samples of one or more alloys. In table 2-1 the names of the alloys used in this chapter are shown.

Table 2-1 Alloys used in this part of the study.

Alloy	Alloy condition	Manufacturer
Degulor C	AC	Degussa, Frankfurt, FRG
Apollo IV	AC	Elephant Edelmetaal BV, Hoorn, the Netherlands
Protor 3	AC	Cendres et Métaux SA, Bienne, Switzerland
Oralit	AC	Schöne, Amsterdam, the Netherlands
Minerva 3S	AC	Elephant Edelmetaal BV, Hoorn, the Netherlands
Medior	AC	Cendres et Métaux SA, Bienne, Switzerland
Pontallor 3	AC	Degussa AG, Frankfurt, FRG
Mirafort 3	AC	Elephant Edelmetaal BV, Hoorn, the Netherlands
Auropall IV	AC	Wieland Edelmetalle GmbH, Pforzheim, FRG
Pallorag 33	AC	Cendres et Métaux SA, Bienne, Switzerland
Phöbus Guss	AC	Wieland Edelmetalle GmbH, Pforzheim, FRG
Palliag M	AC	Degussa AG, Frankfurt, FRG
Pallium 3	AC	Elephant Edelmetaal BV, Hoorn, the Netherlands
WLW	AC	Williams Gold Ref Co, Buffalo, USA
Degudent U	AC, F	Degussa AG, Frankfurt, FRG
A32	AC, F	Austenal Dental, Köln, FRG
Orion WX	AC, F	Elephant Edelmetaal BV, Hoorn, the Netherlands
Deva M	F	Degussa AG, Frankfurt, FRG
NP_2	AC, F	Austenal Dental, Köln, FRG
Wiron 77	F	Bego, Bremen, FRG
Wiron 88	F	Bego, Bremen, FRG
Unibond Forte	F	Unitek Co, Monrovia, USA
Talladium	AC, F	Talladium Inc , Annaheim, USA
Vicomp	AC, F	Austenal Dental, Köln, FRG

AC. as cast, F. simulated porcelain-firing condition

To get a more accurate insight into the chemical composition of the alloys included in this investigation, electron probe X-ray microanalysis was executed* In *appendix 1a and 1b* background information on the technique and problems related to the measuring procedure are given. X-ray diffraction provides a means to verify the crystal structure of an alloy. It is used in the chapters 4-6 to detect different phases and their lattice characteristics In *appendix 2* technical details about this method are shown.

The tables 2-2 and 2-3 comprise the chemical composition of the respective alloys investigated in this part of the study.
In general, these tables give an impression of the chemical composition of the alloy gamut available at the start of this study Slight differences from manufacturers data may occur due to accidental casting pollution in crucibles previously used for other alloys. New alloy developments are discussed separately in the chapters 4 to 6.

Table 2-2 Chemical composition (wt%) of the type III/IV casting alloys used in this investigation, as determined by electron probe X-ray microanalysis Standard deviations are given between brackets

a) Class 3, high gold, type III/IV casting alloys satisfying the ADA specification

Alloy	Pt	Au	Ag	Pd	Cu	Zn	Balance
Degulor C	2 3 (0 5)	74 6 (0 4)	13 4 (0 2)	1 5 (0 3)	7 3 (0 3)	0 7 (0 3)	Fe, Ni
Apollo IV	4 2 (0 3)	70 2 (0 5)	13 4 (0 4)	1 8 (0 2)	9 2 (0 6)		Co, In, Zn, Sn
Protor 3	2 6 (0 5)	68 3 (0 9)	12 1 (0 4)	3 5 (0 4)	11 3 (0 6)	1 9 (0 1)	Co, Ni, In, Sn

* Camebax type MBI Cameca, Paris, France and Tracor Northern, Middleton, USA

b) Class 2, medium gold, type III/IV alloys.

Alloy	Au	Ag	Pd	Cu	In	Zn	Sn	Balance
Oralit	59 4 (1.8)	27.9 (0 5)	5 0 (0.7)	5 7 (0.4)		1 6 (0 2)		Ni, Fe, Sn
Minerva 3S	55.5 (0.6)	27.4 (0 6)	6.5 (0 5)	8.1 (0.3)				Pt, Co, Fe, Ni, In, Sn, Re
Medior 3	54 5 (1.0)	25.8 (0.5)	5 7 (0.1)	11 2 (0.5)		1 8 (0.3)		Pt, Co, Ni, Fe, Ga, Sn
Pontallor 3	42.0 (1 8)	38 9 (1.3)	6.4 (0.6)	4.1 (0.4)	4.5 (0.5)	1 9 (0.7)	1.9 (0.1)	Fe, Ni

c) Class 1, low gold, type III/IV alloys.

Alloy	Au	Ag	Pd	Cu	In	Zn	Sn	Balance
Mirafort 3	39,4 (0.5)	39,8 (0.7)	6,3 (0.3)	4,0 (0.3)	5,4 (0 6)	1,9 (0.4)	2 7 (0.7)	Co, Fe
Auropall IV	39.1 (0.3)	46.5 (0.7)	5 9 (0 3)	6.5 (0.3)		1.1 (0.4)		Pt, Co, Fe, Ga, In, Sn

d) Class O, no gold, type III/IV alloys.

Alloy	Au	Ag	Pd	Cu	In	Zn	Balance
Pallorag 33	11.1 (0.6)	5 7 (2)	20.4 (0.8)	10.4 (0 5)			Co, Ni, Zn, Sn
Phobus Guss	10.2 (0 4)	54.4 (0.6)	19.8 (0.6)	14.9 (0.2)			Pt, Co, Fe, Ni, Sn
Palliag M	2 8 (0 3)	57.1 (1 4)	26.5 (0.3)	11.5 (0.7)		1.2 (0.7)	Pt, Co, Ni, Sn,
Pallium 3	2 3 (0.1)	59.7 (1.2)	25.5 (0.4)	10.2 (0.6)		1.2 (0.3)	Pt, Co, Cr, Ni, In, Sn
WLW		70.1 (0.6)	25 0 (0.6)		3.5 (0.4)		Pt, Au, Cu, Ni, Mo

Table 2-3 Chemical composition (wt%) of the PFM alloys used in this investigation as determined by electron microprobe. Standard deviations are given between brackets.

a) Au-Pt-Pd and Au-Pd(-Ag) alloys

Alloy	Pt	Au	Ag	Pd	Sn	In	Ga	Balance
Au-Pt-Pd								
Degudent U	10 2 (0 7)	77 0 (1 2)	1 5 (0 5)	8 9 (0 4)		1 1 (0 2)		Cu, Fe, Sn, Zn
Au-Pd(-Ag)								
A32		50 8 (0 7)		37 1 (0 7)		9 5 (0 6)	1 8 (0 3)	Cu, Fe, Zn, Ru
Orion WX		49 2 (0 1)	1 4 (0 8)	38 2 (0 9)		8 9 (0 5)	1 92 (0 08)	Cu, Fe
Deva M		46 1 (0 4)		44 5 (0 3)	9 2 (0 1)			Cu, Fe, Ni

b) Ni-Cr(-Be) alloys.

Alloy	Ni	Cr	Fe	Mo	Ga	Al	Si	Be	Balance
NP_2	66 5 (0 8)	13 15 (0 12)	5 2 (0 2)	7 2 (0 4)	6 8 (0 7)				Co, In, Mn
Wiron 77	66 3 (0 4)	22 0 (0 3)			6 7 (0 3)		4 0 (0,1)		Pd, Cu, Fe, Mn, Ga, Sn
Wiron 88	60 0 (0 4)	25 1 (0 4)	1 9 (0 2)	10 1 (0 3)			2 1 (0 2)		Pd, Ag, Co, Mn, Sn
Unibond Forte*	64	22	1	9					Nb + Ta 4%
Talladium	71 9 (0 5)	14 4 (0 3)		8 6 (0 1)		2 4 (0 3)		2 1	Pt, Fe

* values given by manufacturer

c) Co-Cr alloy composition (wt%) as determined with a Jarrell-Ash 900 emission spectrometer (Jarrell-Ash, USA).

Alloy	Cr	Co	Mo	Mn	C	Si	B
Vicomp	32 0*	61 1*	5 6	0 5	0 02	0 05	0 1

* values given by manufacturer

2.2 The corrosion technique used in this study

2.2.1 Introduction

Corrosion phenomena in aqueous environments like saliva may be explained in terms of electrochemical reactions. Measurement of current-potential relations carried out under carefully controlled conditions may yield information on the corrosion rates, pitting tendency and the ability of a certain metal or alloy to passivate. Electrochemical testing procedures are generally accepted in technical applications to produce (relatively) rapid results. They were originally designed for industrial research in general rather than for the investigation of dental casting alloys. To measure corrosion characteristics on a more refined level, sophisticated electrochemical techniques are needed.

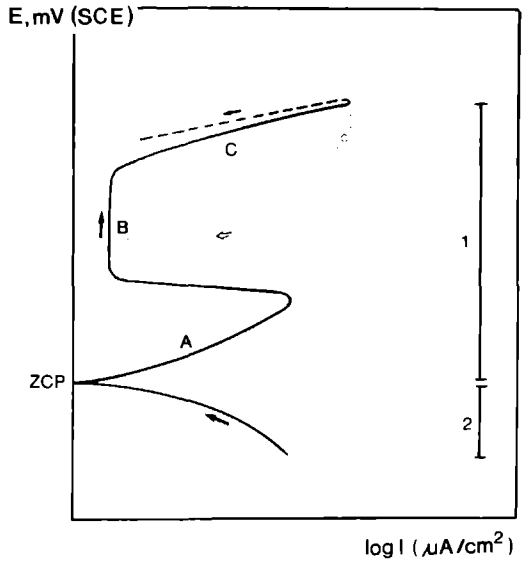
It is difficult to simulate the oral environment. Its complexity is reflected in the great number and variety of electrolytes proposed for dental corrosion laboratory research. They range from simple solutions containing various amounts of aggressive anions (e.g. chloride ions) to complex artifical salivas (Darvell, 1978; Marek, 1983). The last category includes buffering components and mucin-like proteins in order to take the protective mechanisms of the oral environment into account. Various pH values and degrees of (de-)aeration are advocated (Greener and Matsuda, 1985; Geis-Gerstorfer *et al*, 1986).

Electrochemical aspects in corrosion testing also vary considerably. This is reflected in the scan rates of polarization measurements, the way of inducing a potential (continuous dynamic or stepping followed by a period of equilibration) and the testing range covered. Results of this variety of testing procedures and environments doubtlessly add to the knowledge of various aspects of oral corrosion phenomena. However, findings are often conflicting, just as the relevance for the clinical situation of any laboratory test is open for debate. Although many alloys have been investigated, test differences make it difficult to combine the results of the small number of alloys investigated in the distinct studies.

The previous remarks strongly suggest a larger selection of alloys covering the present dental field. Furthermore, the use of generally accepted testing procedures in more than one electrolyte is recommendable. Thus a comparison (within the limitations of a laboratory set-up) is within reach. In the following, a number of testing aspects relevant to this investigation will be pointed out.

Potentiodynamic (cyclic) polarization is a means of characterizing a metallic specimen by its current-potential relationship. In this type of experiment one measures polarization characteristics by plotting the current response (per square surface unit) as a function of the applied potential. As current density may vary over several orders of magnitude, a log representation of the current density is generally accepted. In this way the area in which corrosion behaviour is activation polarization controlled, will show as a sharp linear current density increase with a low slope: the zone of Tafel behaviour.

Different areas may be distinguished in the anodic part of the forward polarization scan (fig. 2-1), depending on the metal and the electrolyte involved. The active



A : active region
B : passive region
C : transpassive region
ZCP : zero current potential
1 : anodic part of the polarization scan
2 : cathodic part of the polarization scan
--- : reverse scan indicating reversible behaviour
ooo : reverse scan indicating prolonged attack

Fig. 2-1 Schematic polarization diagram of a passivating alloy.

region is indicated by a sharp linear anodic current density increase: the metal corrodes progressively with anodic polarization.
The onset of passivity is indicated by a sharp decrease of current density upon further anodic polarization. The current density becomes low but is still measurable. It is necessary to maintain the protective passive film. Further polarization may lead to a transpassive region where the passive film is progressively attacked and current density tends to increase rapidly. Reversing the scan direction, the current density response may provide information about reversibility of the electrochemical behaviour or phenomena associated with pitting or lack of protective film (fig. 2-1).
During a polarization resistance measurement a limited potential scan (25 mV) around the open circuit potential (OCP) is performed. A linear relationship between overvoltage ($\triangle$ E) and external current ($\triangle$ I) is found around the OCP. The OCP is the potential where an isolated metallic specimen is in equilibrium with the specific aqueous environment. A metal with a high or 'noble' OCP will not easily become an anode, i.e. open to a potentially corrosive action. The equilibrium condition at OCP implies that anodic and cathodic reactions occur at the same rate and no net external current is measurable.
In an equilibrium condition there is no external current when the alloy specimen is functioning in an isolated situation, Thus special methods are necessary to determine the corrosion current density (I_{corr}).

According to Steam and Geary (1957):

$$I_{corr} = \frac{(\beta_a \beta_c)}{2.3\,(\beta_a + \beta_c)} \cdot \frac{1}{R_p}$$

Here Rp is the polarization resistance ($\triangle$ E / $\triangle$ I), while β_a and β_c are the anodic and cathodic Tafel slopes respectively. I_{corr} can be used as a measure of corrosion resistance of an alloy functioning under equilibrium conditions.
Tafel slopes can be derived using separate so-called Tafel plots. Polarizing the metal specimen up to 300 mV anodically and cathodically from the open circuit potential, the logarithmic relation between applied potential and resulting current density occurs, providing the reactions are activation polarization controlled. A sharp linear current density increase with a low slope, the Tafel slope, shows when activation controlled polarization excursions exceed $\pm$ 25 mV from equilibrium conditions (Scully, 1981).
Well accepted electrochemical techniques of in vitro corrosion measurement provide means of gathering information in a relatively rapid way. A comparison of a great number of samples of alloy systems under various conditions is thus within reach.

2.2.2 Experimental design

Disc-like specimens (15 mm diameter x 2 mm) of the alloys used (table 2-1), were made according to the instructions of the manufacturer. The specimen size was chosen to represent an upper limit to the clinical thickness requirement of the occlusal aspect, with the understanding that it would represent a limiting situation for thermal and mass diffusion processes depending on cooling rate. In order to simulate general practice conditions, all specimens were cast commercially using manufacturers' instructions. All PFM-alloys used, received a simulated porcelain-firing heat treatment (F), consisting of an oxidation treatment, one opaque and two gingival porcelain-firings under vacuum, as well as a glazing procedure at ambient air pressure. Time and temperature for these procedures are specific for each alloy-porcelain combination. Moreover, some selected PFM-alloys were additionally tested in the as cast condition (AC) because some technicians utilized PFM-systems in the as cast condition as a type IV substitude. All type III/IV alloys were investigated in the AC-condition.
Specimens were ground through 800 grit silicon carbide paper under running tap water and subsequently polished through a 1/4 μm alumina paste prior to immersion into the corrosion cell. Cleaning after polishing was performed ultrasonically in acetone for two minutes (organic debris removal), followed by an ultrasonic treatment during five minutes in distilled water.
A standard specimen holder (K0105, EG & G, Princeton, USA) exposing 1 cm^2 of polished surface was employed in conjunction with a standard corrosion cell (ASTM Specification G5-69). A saturated calomel (SCE) electrode (K0105, EG & G, Princeton, USA), including a salt brige was used as a reference electrode. The counter electrode consisted of 2 symmetrically placed carbon rods. Testing was carried out in two different electrolytes: a 0.9% saline solution (pH = 5.5) and an artificial saliva (pH = 5.3) according to Meyer and Nally (1975a,b). The chemical composition of the artificial saliva is given in table 2-4.

Table 2-4 The chemical composition of the artificial saliva according to Meyer and Nally (1975a,b).

NaCl	0 400 g
KCl	04 00 g
$CaCl_2$ $2H_2O$	0 795 g
NaH_2PO_4 H_2O	0 690 g
Na_2S $9H_2O$	0 005 g
Urea	1 0 g
Aqua Dest	ad 1000 ml

The saline solution was selected because it represents an aggressive solution without inhibitory action. The artificial saliva reportedly produces corrosion results closer to those obtained for natural saliva (Meyer and Nally, 1975b). All tests were run at an ambient temperature of 23°C. Both testing solutions were unstirred (stagnant) and they were exposed to air prior to and during testing. All measurements were performed with a potentiostat/galvanostat (model 273, EG & G, Princeton, USA) connected to an Apple IIE computer. A dedicated software package (Softcorr, EG & G, Princeton, USA) provided facilities to run the test automatically and evaluate the results obtained.

Testing procedures for each specimen consisted of two polarization runs, interrupted by re-polishing. During the first sequence, the open circuit potential (OCP) was monitored as a function of time for at least one hour. This part of the test was continued until there was no detectable change in OCP for at least 2 minutes. Subsequently, a potential scan was run from −20 mV (SCE) to +20 mV (SCE) around OCP at a scan rate of 0.1 mV/s to obtain data for a polarization resistance calculation. It was followed by a potential scan from −250 mV (SCE) to +250 mV (SCE) around OCP at a scan rate of 0.2 mV/s to provide data for a Tafel-constant calculation. After repolishing, a second sequence produced a potentiodynamic hysteresis profile from −1000 mV (SCE) to + 1000 mV (SCE) at a scan rate of 0.5 mV/s. Before this test, the sample was held at −1000 mV (SCE) for 10 minutes to remove surface oxide films. Scan rates were chosen to be of the same order as those recommended by ASTM and yet allow the convenient collection of the data. These scan rates were consistent with those used by the author previously (Mezger *et al.*, 1985, 1986; Vrijhoef *et al.*, 1987).

Generally, I_{corr} values were computed by means of the dedicated software package (Softcorr, EG & G, Princeton, USA). A traditional graphical extrapolation method (Scully, 1981) was used in those cases where the software method broke down, e.g. because of sponteneous passivation. In such a case, the cathodic Tafel-line was extrapolated to the zero current potential (ZCP), i.e. E (I = 0). I_{corr} values as derived from the distinct Tafel scans were double-checked with the I_{corr} values calculated from the polarization resistance scans.

Duplicate, triplicate and more measurements were executed fo. at least 25 alloy-alloy condition combinations per electrolyte. Based on these data, calculations of the precision of the measurements were performed.
The first problem in specifying measurement errors is the choice between absolute error or relative (%) error. The decision for this specification was made according to the scattergram of the mean observed value against the absolute (standard deviation of the duplicate or triplicate) or the relative difference (standard deviation/mean). A zero correlation of the mean with the absolute differences in combination with a negative correlation with the relative differences indicates absolute errors to be constant. A positive correlation of the mean with the absolute difference and a zero correlation with the relative differences leads to a specification of a constant relative error.
In this study it turned out that the errors in the potential values had to be specified absolutely (in mV) and the errors in the current densities relatively (%). The overall error is calculated using the weighted mean of the individual error variances (weighting according to the degrees of freedom of the individual error variance, $n-1$).
The errors observed in measurements done in 0.9% saline solution or artificial saliva were comparable, so differentiation according to electrolyte was not necessary.
Due to the variety of alloys the variation in the measurements was very large. For this reason it was impossible to estimate the error in extreme measurement results. The errors calculated in the study are based on a range comprising about 90% of the measurements.
The calculated measurement errors and the corresponding ranges are presented in table 2-5.
A global conclusion drawn from table 2-5 may be that the error in potential value is about 60 mV and in the current densities 50%. The impression exists that errors in measurements beyond the specified ranges are larger.

Table 2-5 Calculated measurement errors and the corresponding ranges of individual results of the alloys presented in this chapter.

Parameter	Range	Measurement error
ZCP	(-350, -20)mV	68 mV
OCP	(-300, 160)mV	54 mV
I_{corr}	(0.02, 0 60) $\mu A/cm^2$	54%
I_{100}	(1, 6) $\mu A/cm^2$	50%
I_0	(0 2, 15) $\mu A/cm^2$	44%
I_{100}	(0.7, 30) $\mu A/cm^2$	48%
I_{200}	(1.1, 30) $\mu A/cm^2$	48%
I_{300}	(1.2, 30) $\mu A/cm^2$	48%
I_{400}	(1 2, 35) $\mu A/cm^2$	44%
I_{500}	(1.7, 70) $\mu A/cm^2$	50%

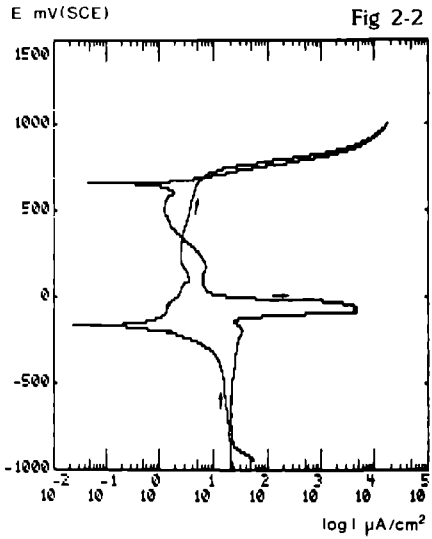


Fig 2-2

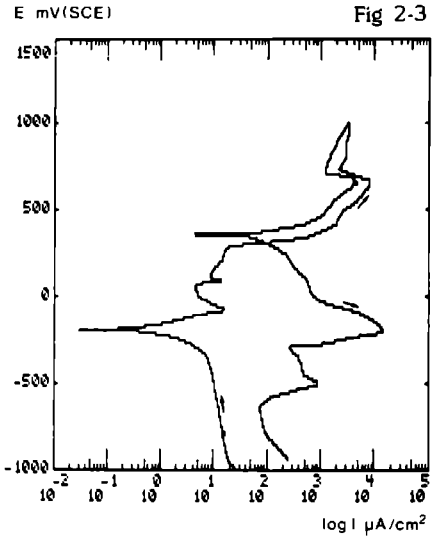


Fig 2-3

Fig. 2-2 Cyclic polarization diagram of Protor 3 (AC) in 0.9% saline solution.

Fig. 2-3 Cyclic polarization diagram of Pallium 3 (AC) in 0.9% saline solution.

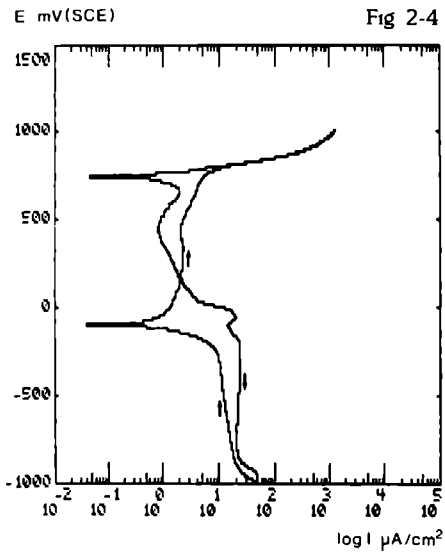


Fig 2-4

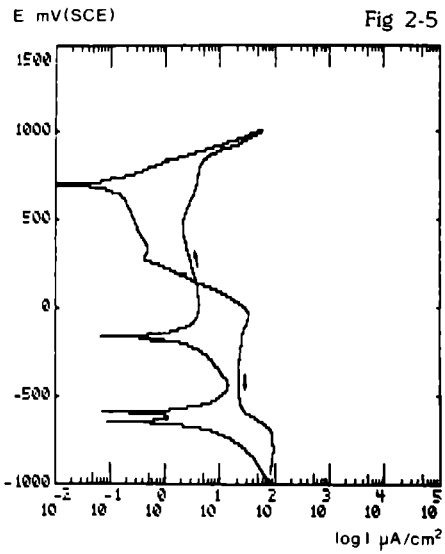
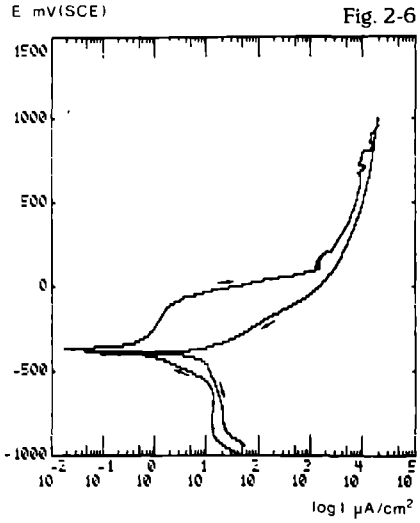


Fig 2-5

Fig. 2-4 Cyclic polarization diagram of Degudent U (F) in 0.9% saline solution.

Fig. 2-5 Cyclic polarization diagram of A 32 (F) in artificial saliva.



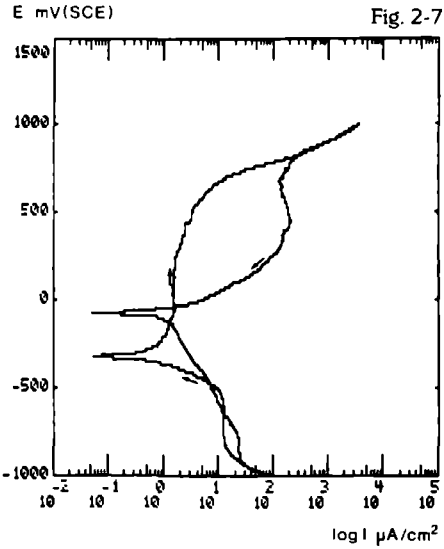
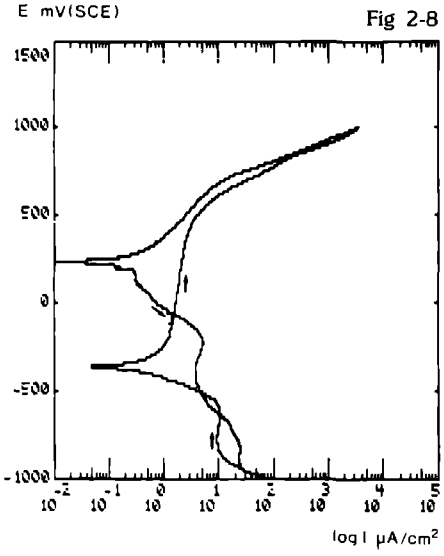


Fig. 2-6 Cyclic polarization diagram of Talladium (F) in 0.9% saline solution.

Fig. 2-7 Cyclic polarization diagram of NP_2 (F) in 0.9% saline solution.



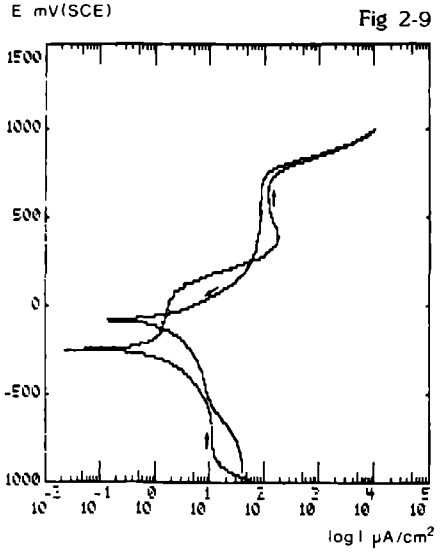


Fig. 2-8 Cyclic polarization diagram of Unibond Forte (F) in 0.9% saline solution.

Fig. 2-9 Cyclic polarization diagram of Wiron 88 (F) in 0.9% saline solution.

2.3 Results

Typical cyclic polarization diagrams for the different alloy groups are given in figs. 2-2 to 2-9. In table 2-6 the alloys used in this chapter and the representative cyclic polarization diagrams are correlated.
Electrochemical data on the alloys used in both testing solutions are presented in *appendix 3* (tables 2-7 to 2-18).

Table 2-6 Alloys used in this chapter and the cyclic polarization diagram representing its general appearance in the respective electrolytes.

Alloy	Condition	0.9% saline	Artificial saliva
Degulor C	AC	Fig. 2-2	Fig 2-2
Apollo IV	AC	„ 2-2	„ 2-2
Protor 3	AC	„ 2-2	„ 2-2
Oralit	AC	„ 2-2	„ 2-2
Minerva 3 S	AC	„ 2-2	„ 2-2
Medior 3	AC	„ 2-2	„ 2-2
Pontallor 3	AC	„ 2-2	„ 2-2
Mirafort 3	AC	„ 2-2	„ 2-2
Auropall IV	AC	„ 2-2	„ 2-2
Pallorag	AC	„ 2-3	„ 2-3
Phobus Guss	AC	„ 2-3	„ 2-3
Palliag M	AC	„ 2-3	„ 2-3
Pallium 3	AC	„ 2-3	„ 2-3
WLW	AC	„ 2-3	„ 2-3
Degudent U	AC + F	„ 2-4	„ 2-4
A 32	AC + F	„ 2-4	„ 2-5
Orion WX	AC	„ 2-4	„ 2-4
Orion WX	F	„ 2-4	„ 2-5
Deva M	F	„ 2-4	„ 2-5
NP_2	AC	„ 2-7	„ 2-7
NP_2	F	„ 2-7	„ 2-8
Wiron 77	F	„ 2-6	„ 2-6
Wiron 88	F	„ 2-9	„ 2-9
Unibond Forte	F	„ 2-8	„ 2-8
Talladium	AC + F	„ 2-6	„ 2-6
Vicomp	AC + F	„ 2-8	„ 2-8

AC: as cast, F: simulated porcelain-firing condition

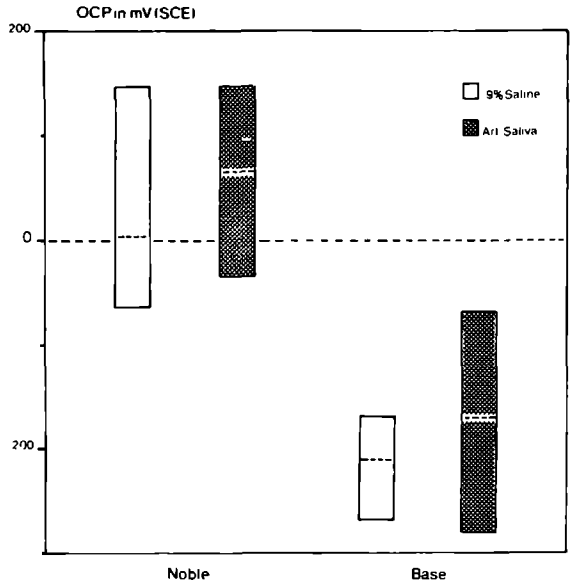


Fig 2-10 Minimum and maximum values of the open-circuit potential (OCP) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

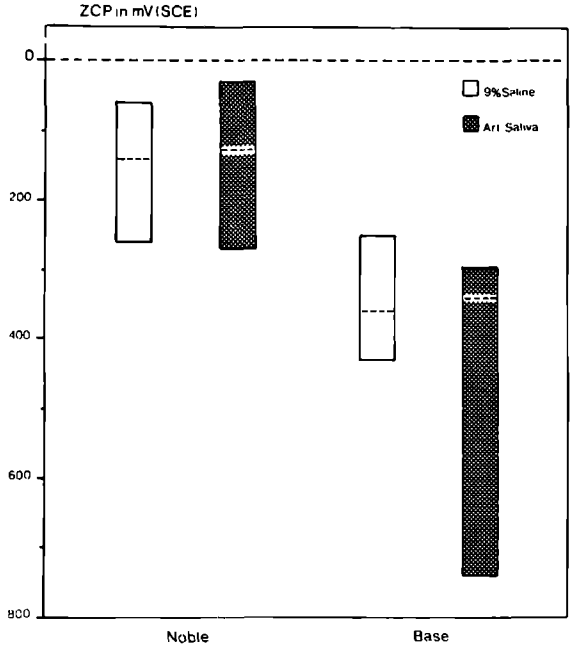


Fig. 2-11 Minimum and maximum values of the zero current potential (ZCP) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

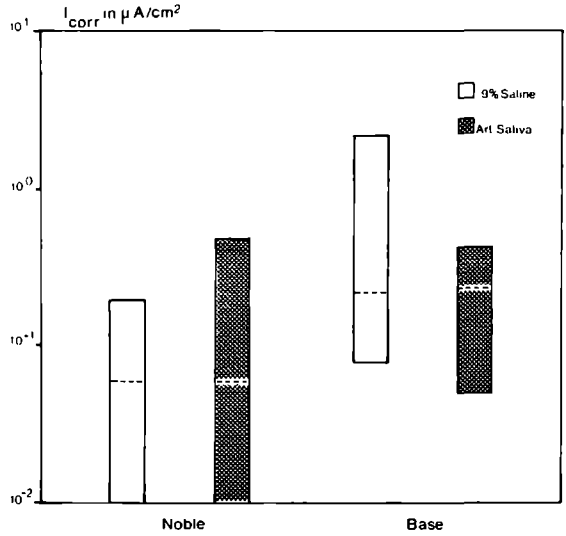


Fig. 2-12 Minimum and maximum values of the corrosion current density (I_{corr}) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

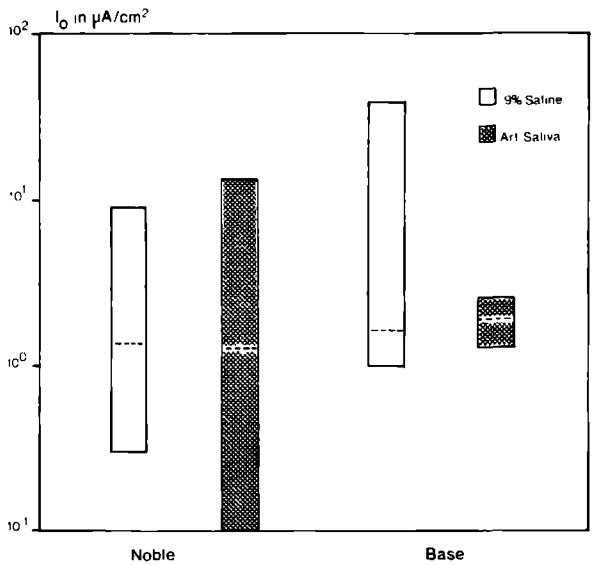


Fig. 2-13 Minimum and maximum values of the current density at 0 mV (SCE) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

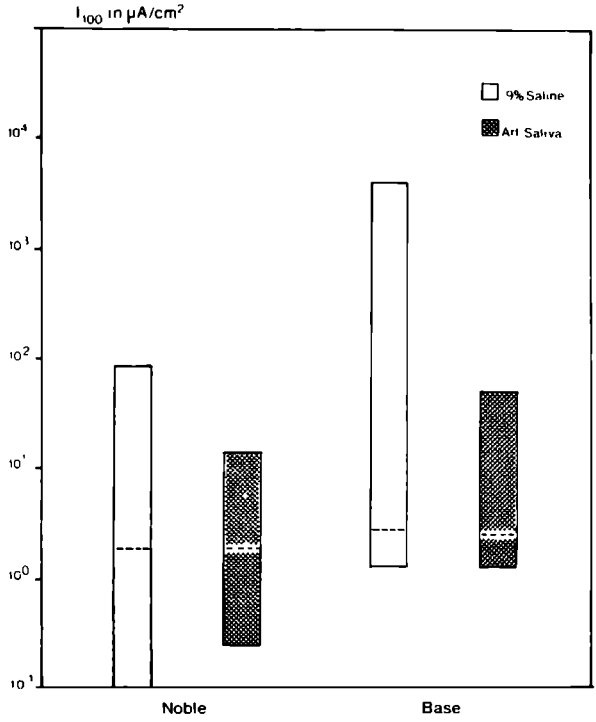


Fig. 2-14 Minimum and maximum values of the current density at +100 mV (SCE) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

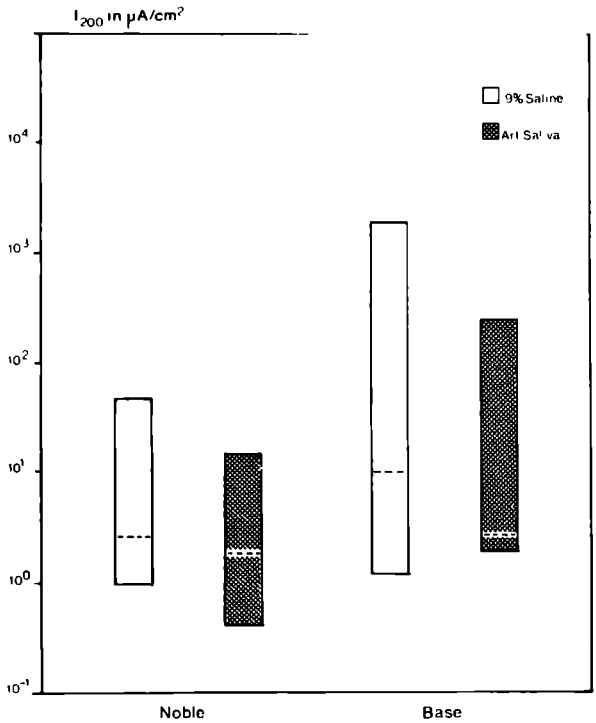


Fig. 2-15 Minimum and maximum values of the current density at +200 mV (SCE) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

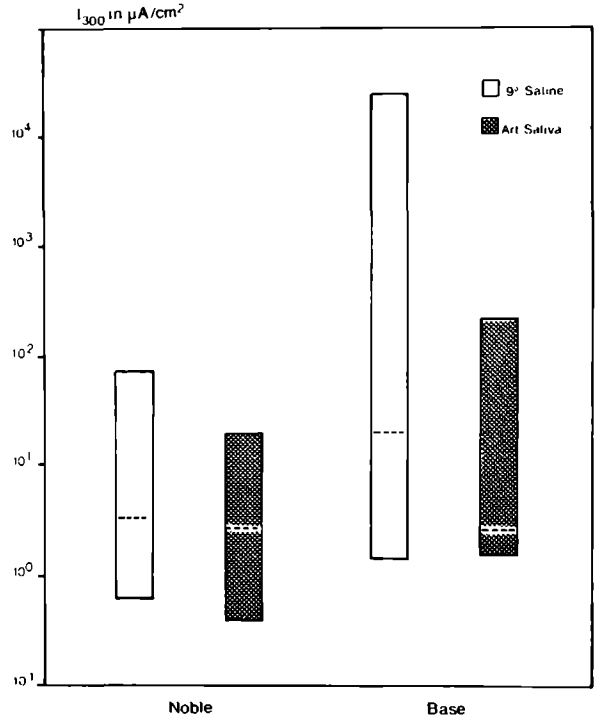


Fig. 2-16 Minimum and maximum values of the current density at +300 mV (SCE) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

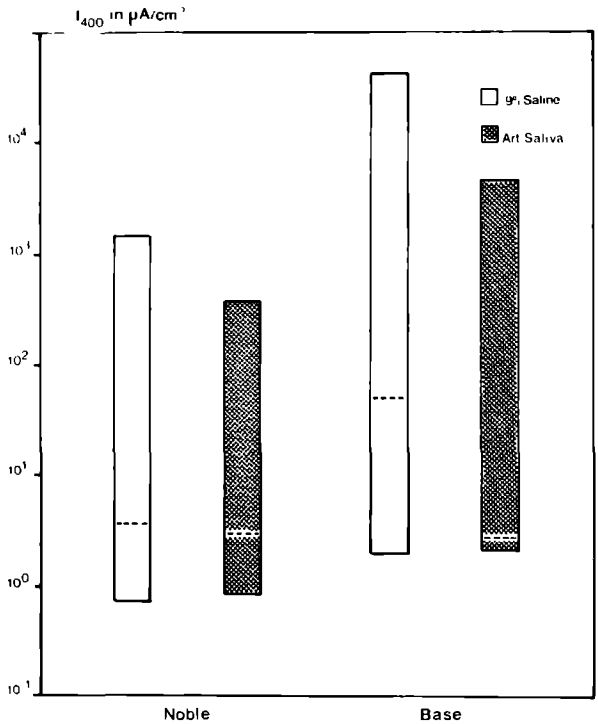


Fig. 2-17 Minimum and maximum values of the current density at +400 mV (SCE) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

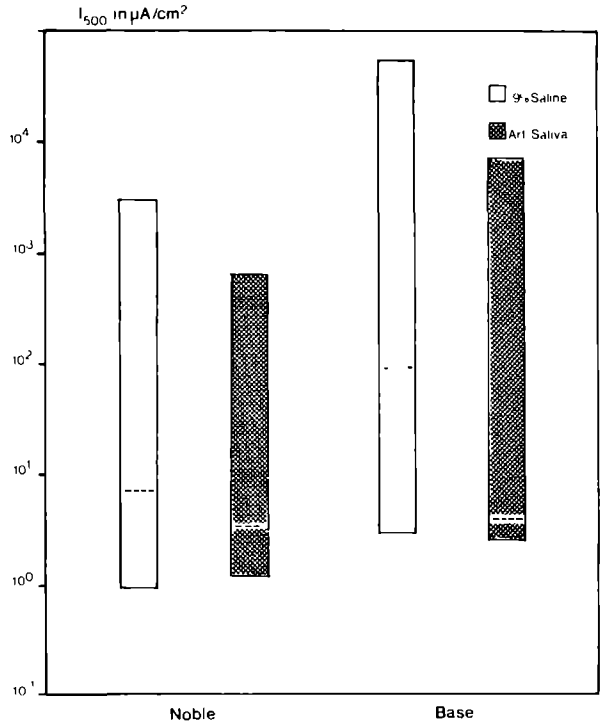


Fig. 2-18 Minimum and maximum values of the current density at +500 mV (SCE) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

The current density values in the tables 2-7, 2-8, 2-11, 2-12, 2-15 and 2-16 are derived from one cyclic polarization diagram for each alloy. The diagram was chosen at random from the replications made. The OCP and ZCP were selected in a similar way. In the tables 2-7 to 2-18 the results are shown according to alloy type. A subset of the porcelain-bonding alloys is additionally tested in the as cast condition. As it has been stated previously, these alloys are used in this condition for full and partial veneer crown castings.
To visualize some trends figs. 2-10 to 2-18 depict the corrosion data variation for noble and base metal alloys in both electrolytes. In all cases minimum, maximum and median values are shown.
In both electrolytes, the OCP and ZCP tend to lower potential values for the base metal alloys. The highest I_{corr} values occur for some base metal alloys, especially in 0.9% saline solution. In both solutions the median values for these alloys are also higher.
The data derived from the cyclic polarization scans show an early anodic current density increase in 0.9% saline solution for Talladium (AC and F), Wiron 77 F and to a lesser extent for WLW (AC), Wiron 88 (F) and NP_2 (AC) as well.

For the class O type III/IV alloys generally a distinct current density increase is found around +300 mV (SCE). The other alloys show this increase at higher potentials in 0.9% saline solution.

In artificial saliva, a steep anodic current density increase generally starts at higher anodic potential values than in 0.9% saline solution. Similarly, current densities at scan reverse usually are lower. No actual breakdown occurs for the Au-Pt-Pd and Au-Pd-(Ag) alloys. For Talladium, in both AC and F condition, already below +200mV (SCE) sharp current density increases were found. For some base metal alloys higher current densities were found in the anodic part of the reverse scan, than those at corresponding forward scan potential values. In 0.9% saline solution this occurs for NP_2 (AC and F), Wiron 77 (F) and Talladium (AC and F). In artificial saliva the same behaviour is found for NP_2 (AC), Wiron 77 F and Talladium (AC and F).

In artificial saliva the alloys NP_2 (AC), Unibond (F), Vicomp (AC and F), A 32 (AC and F), Orion WX (F) and Deva M (F) give evidence of cathodic loops in the cathodic part of the forward scan (see e.g. fig. 2-5).

Figs. 2-13 to 2-18 show that the median current densities of noble and base metal alloys in artificial saliva are equivalent. Those for noble systems appear not to be influenced by replacing artificial saliva with 0.9% saline until overpotentials exceeding 400 mV (SCE). However, the median current density values of base metals turn out to be higher in 0.9% saline solution compared to artificial saliva.

Figs. 2-19 shows the extreme localized attack on Talladium (F) after cyclic polarization in 0.9% saline solution. Talladium (AC and F) in both electrolytes and to a lesser extent Wiron 77 (F) and NP_2 (AC) in 0.9% saline solution show signs of crevice corrosion at the margin of the exposed alloy surface in the specimen holder.

Fig. 2-19 Talladium (F) sample after cyclic polarization testing in 0.9% saline solution. Note the material removed at the border of the exposed alloy surface.

2 4 Discussion

The primary interest of the corrosion data presented in this chapter is to describe an armamentarium of currently available alloys Hereby, a subsequent comparison between new developments and the already existing, accepted systems becomes possible Too detailed a discussion in terms of a correlation with chemical composition and microstructure is beyond the scope of this study In chapter 4 to 6 it will be shown where the new alloy developments investigated are situated On the basis of such a comparison, the relative corrosion risks in the clinical situation will be forecasted and further investigated in chapter 7

In both electrolytes, the OCP values for all alloys are higher than the corresponding values for the ZCP This discrepancy may be related to the formation of a thin film after polishing or upon direct immersion Cathodic polarization at −1000 mV (SCE) is expected to reduce some of this film or eliminate it Consequently, ZCP will be lower than OCP The ZCP of base metals tends to be lower than for noble alloys, although some overlap exists (fig 2-11) Therefore, generalizations as to differences between the respective types of alloys should be omitted

I_{corr} indicates the corrosion behaviour of an alloy acting in an isolated condition The highest I_{corr} values occur for some base metal alloys in 0 9% saline solution The median I_{corr} value in both solutions shows this tendency as well However, the I_{corr} of other base metal alloys is situated among the lower ones of the whole group of alloys So no general trend may be derived In artificial saliva the minimum and maximum I_{corr} values differ less than in 0 9% saline solution This is consistent with the fact that this solution is less aggressive

The data from the cyclic polarization diagrams should be regarded with the area of oral interest' (Ewers and Greener, 1985, Corso *et al* , 1985) in mind More specifically its presumed anodic boundary value of +300 mV (SCE) deserves attention Below this potential value, a lower anodic current density, as an indication for ion-releasing activities, gives a better prognosis Data from the cyclic polarization diagrams, as summarized in the tables 2-7 to 2-16 (*appendix 3*), show that the 0 9% saline solution is markedly more aggressive than the artificial saliva Especially in the base metal group it brings about a substantial separation between alloys The influence of the corrosion medium gives some indication of the individual patient factor

In 0 9% saline solution the Ni-Cr-Be alloy Talladium and the Ni-Cr alloy Wiron 77 break down well within the supposed fail-save zone Phobus Guss (AC) shows a fairly early increasing current density, but a real breakdown occurs around +300 mV (SCE) To a lesser extent this holds true for WLW (AC) and Wiron 88 (F) As a whole, the class O type III/IV alloys form an intermediate group For the other alloys, the current density increase starts well away from the anodic boundary of the area of oral interest, thus allowing more severe anodic overloading The hysteresis loop indicated by current density increase after scan reverse, heralds a non reversible electrochemical behaviour or phenomena associated with pitting or lack of protective film under unfavourable conditions for some base metal alloys In 0 9% saline solution, Talladium AC and F and Wiron 77 F show this behaviour

after an anodic breakdown within the area of oral interest. This indicates a possibility of local corrosion attack under clinical conditions. A hysteresis loop occurring after extreme anodic overloading, combined with a breakdown potential well above the area of oral interest (in case of NP_2 AC and F), most presumably has no direct clinical relevance. Crevice corrosion evidences local in vitro attack on specimens of Talladium AC and F (fig. 2-19) and less severely, also on NP_2 AC and Wiron 77 F.
In artificial saliva, an electrolyte considered to be less aggressive, the current density increase in the anodic part of the forward scan occurs at higher potential values. Talladium, the Ni-Cr-Be alloy, breaks down well within the area of oral interest and shows a hysteresis loop in both alloy conditions.
In artificial saliva irreversible electrochemical behaviour also occurs for some other base metal alloys under extreme conditions (Wiron 77 F, NP_2 AC). In the simulated fired condition NP_2 does not show this tendency.
Sometimes cathodic loops occur in the forward scan (see e.g. fig. 2-5). In this study they are related to alloys otherwise acting favourably in the tests (NP_2 AC excluded). Cathodic loops indicate that the alloy specimen involved, does not 'know' whether to behave as an anode or a cathode.

2.5 Summary

A corrosion data base of current dental casting alloys has been created using accepted electrochemical techniques and two electrolytes. Results indicate that under laboratory conditions not only the nobility of components in the alloys, but also passivating tendencies play an important role. Large differences occur within the base metal alloy group.
This data base will serve as a reference for the corrosion profiles of the new alloy development of the chapters 4 to 6.

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CHAPTER 3

Effect of mucin on the corrosion behaviour of dental castings alloys*

P.R. Mezger
M.A. van 't Hof
M.M.A. Vrijhoef
E.J. 's Gravenmade
E.H. Greener

Abstract

The influence of mucin on the corrosion behaviour of seven typical dental casting alloys was investigated. A commercial saliva substitute (Saliva Orthana®) containing mucin and a control from which the mucin was removed, were used.
The electrochemical behaviour of the test alloys was evaluated around the open circuit potential (OCP), utilizing standard potentiodynamic techniques, as a function of oxygen concentrations and pH.
The results of the corrosion measurements were analyzed by a 4-way ANOVA to detect the influence of alloy, environment and possible interactions. Mucin seems to act as a cathodic inhibitor at pH = 6.7 but not at pH = 4.6.
An unidentified component (e.g. benzoate) of the saliva substitute probably acts as an adsorption inhibitor. Anodic passivation is correlated with the artificial saliva composition as well.

3.1 Introduction

A sufficient corrosion resistance of metallic restorations under oral conditions is a prerequisite. Lack of corrosion resistance may result in unacceptable discoloration and surface roughness as well as negatively influence the materials properties. Furthermore, corrosion products may adversely influence the biological system (Bergman *et al.*, 1980; Wright and Gallant, 1982).
Human saliva has a complicated and varying composition of inorganic and organic origin (Jenkins, 1978). Aggressive anions such as Cl^-, together with local variations in oxygen tension and pH play a role in the corrosion process. The carbonic acid-bicarbonate system forms the main buffer system in saliva (Lilienthal, 1955).

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It acts as a cathodic corrosion inhibitor, while the phosphate buffer also functions as a protective inhibitor (Palaghias, 1985) Corrosion can also be markedly affected by organic components such as (glyco)proteins (Svare *et al*, 1970, Finkelstein and Greener, 1978, Clark and Williams, 1982, Holland, 1984) Inhibition may occur through adsorption of these saliva components to a metal surface Palaghias (1985) suggested that the acquired pellicle in oral conditions can act as a diffusion barrier for ionic compounds involved in corrosive processes
In case of patients with a suppressed saliva secretion, the corrosion inhibitive functions may be substantially reduced (Tabak *et al*, 1982, Palaghias, 1985) Xerostomic patients attempt to compensate for this lack of salivary flow by using a saliva substitute Artificial salivas are designed to approximate the physico-chemical properties of human saliva as much as possible A new commercial saliva substitute (Saliva Orthana*) does not contain the carbonate/bicarbonate buffer system because of its low stability (Vissink, 1985) An amount of mucin (30 0 g/l) is added to control its desired rheological and wetting properties Taking into account that most contemporary corrosion studies on dental alloys employ artificial salivas without organic components such as mucin (Marek and Topfl, 1986), utilizing Saliva Orthana® as a test electrolyte may more closely model in vivo conditions Therefore, it was the aim of this investigation to evaluate the effect of mucin on the corrosion behaviour of a group of seven typical dental casting alloys relative to the oxygen concentration and the pH

3 2 Materials and methods

Disc-like specimens (15 mm diameter x 2 mm) of the 7 casting alloys (table 3-1) were made according to the instructions of the manufacturer The alloys were

Table 3-1 Casting alloys used in this study

Alloy	Abbreviation	Manufacturer	Alloy condition
Auropall IV	Aur	Wieland, FRG	AC
Ceram W 1	CeW	Williams Gold, Buffalo, USA	F
Orion Vesta	OrV	Elephant Hoorn, the Netherlands	F
Strator 3	Str	Cendres et Metaux SA, Bienne, Switzerland	AC
Talladium	Tal	Talladium Co , Annaheim, USA	F
Trindium	Tri	Trindium, New York, USA	AC
WLW	WLW	Williams Gold Buffalo USA	AC

AC as cast
F simulated porcelain fired

* A/S Orthana Kemisk Fabrik Kastrup, Denmark

chosen to represent a selection from the spectrum of dental casting alloys used internationally. While certain classes of alloys (i.e. Trindium, an alumininium-bronze alloy) may not be regarded as universally popular, they may be found in extensive use in some countries (Nakayama *et al.*, 1984).

The overall chemical composition of the distinct alloys as determined by X-ray microanalysis* is depicted in table 3-2. In order to simulate general practice conditions, all specimens were cast commercially Porcelain-fired-to-metal (PFM) alloys received a simulated porcelain-firing heat treatment according to the manufacturers' guidelines. Testing was carried out in Saliva Orthana® (SO), a saliva substitute (table 3-3), containing purified pig gastric mucin and bovine submandibular mucin Also a control of SO without mucin (P) was used The pH of both solutions was 6 7 To enable testing at pH = 4 6, lactic acid was added to both solutions. For 450 ml of SO, 7 mmol of lactic acid was needed to reach pH = 4 6, while for the same amount of P only 0.6 mmol of lactic acid was added, indicative of the buffering capacity of mucin. The pH was measured before and after each test with a standard pH meter**.

Table 3-2 Chemical composition (wt %) of the distinct alloys investigated. Standard deviations are given between brackets.

Alloy	Au	Ag	Pd	Cu	Ni	Cr	Mo	In	Ga	Sn	Zn	Al	Be	Other ($\Sigma < 1$ 5%)
Aur	39 1 (0 3)	46 5 (0 7)	5 9 (0 3)	6 5 (0 3)							1 1 (0 4)			Pt, Co, Fe, Ga, In, Sn
CeW		36 7 (0 6)	52 5 (0 7)							10 2 (0 7)				Pt, Co, Fe, Ga, In
OrV	2 26 (0 08)		77 9 (0 6)	10 9 (0 4)					8 5 (0 5)					Ag, Co, Ru, Zn
Str	20 0 (0 4)	36 8 (0 5)	21 2 (0 6)					17 7 (0 8)			4 1 (0 3)			Co, Fe, Ru
Tal					71 9 (0 5)	14 4 (0 3)	8 63 (0 13)					2 4 (0 3)	2 1	Pt, Fe
Tri				87 7 (0 6)	1 22 (0 12)							10 1 (0 2)		Ag, Pd, Co, Mo, Fe, In, Mn
WLW		70 1 (0 7)	25 0 (0 6)					3 5 (0 4)						Pt, Au, Cu, Ni, Mo, Al

* Camebax type MBI, Cameca, Paris, France and Tracor Nothern, Middleton, USA

** PHM 82, Radiometer, Copenhagen, Denmark

All tests were run at a temperature of 37 °C. The test solutions were stirred throughout the experiment.
Tests were performed in passively aerated solutions (5.0 mg O_2/l) or under deaerated conditions (< 0.5 mg O_2/l). The oxygen content was measured by means of an Oxygenmeter*. Oxygen was removed by means of bubbling nitrogen through the corrosion cell for at least half an hour prior to and during testing.
Sample preparation and details about the electrochemical testing procedures are described extensively by Vrijhoef *et al.* (1987).

Table 3-3 Composition of Saliva Orthana® (Vissink, 1985).

Components	
Mucins	30 0 g
Xylitol	20.0 g
KCl	1.20 g
NaCl	0.85 g
$MgCl_26H_2O$	0.05 g
$CaCl_26H_2O$	0 20 g
K_2HPO_4	0 35 g
Aqua dest.	ad 1000 ml

An orthogonal 4-way analysis of variance (ANOVA) was applied to detect influences of the factors alloy (A), mucin content (M), oxygen concentration (O) and possible interactions on the electrochemical parameters of the open circuit potential (OCP) and the corrosion current density (I_{corr}). The tests are only valid if the residuals are approximately normally distributed. This was the case for the open circuit potential (OCP) values. For the corrosion current density (I_{corr}) data a log-transformation was necessary to achieve normality. In addition the log-transformation changes additivity into multiplicativity. This implies that while for the open circuit potential absolute differences can be presented, it is necessary to specify relative differences (percentage) for the current density. Significant interactions, as detected by the 4-way ANOVA, were investigated by means of 3-way ANOVAs, holding constant one of the factors involved in the interaction. Main effects are quantified if the p-value is less than 0.05. In order to avoid false significant interactions due to the large number of tests, interactions are only specified when the overall interaction is significant.

* Z 800, Consort Co., Turnhout, Belgium

An analysis of components was executed as described by Duncan (1965) for the fixed model situation
The following levels of significance were used
s^{x} $0.01 \leq p < 0.05$, s^{xx} $0.001 \leq p < 0.01$, s^{xxx} $p < 0.001$, s^{-} $p \geq 0.05$

3.3 Results

The significance level of the main effects and interactions are given in table 3-4 All factors investigated as well as the mucin-pH (M x H) interaction exert a very significant influence on the OCP The factors alloy (A), pH (H) and to a lesser extent oxygen (O), have a significant effect on I_{corr} It is not only of interest whether certain factors and interactions affect the results, but also to what extent In table 3-5 an estimate of the proportion each factor contributes to the overall variance is given Table 3-5 makes it clear that the alloy factor (A) is a major effect in the experimental design However, the other factors as well as the M x H interaction are significant for OCP, while oxygen and pH are significant for I_{corr}

Table 3-4 Results of the 4-way analysis of variance, testing the influence of the factors alloy (A), mucin (M), oxygen (O), pH (H) as well as their interactions

	Factor or interaction				
Variable	A	M	O	H	Overall interaction
OCP	S^{xxx}	S^{xxx}	S^{xxx}	S^{xxx}	S^{xx} (M x H)
I_{corr}	S^{xxx}	S^{-}	S^{x}	S^{xx}	S^{-}

Table 3-5 Analysis of components of variance of the factors and interactions (in % of total variance)

Source of variance	OCP	I_{corr}
Alloy (A)	70 8	54 4
Mucin (M)	6 2	–
Oxygen (O)	4 3	3 1
pH (H)	4 8	4 4
M x H	4 4	–
Residual	9 5	38 1

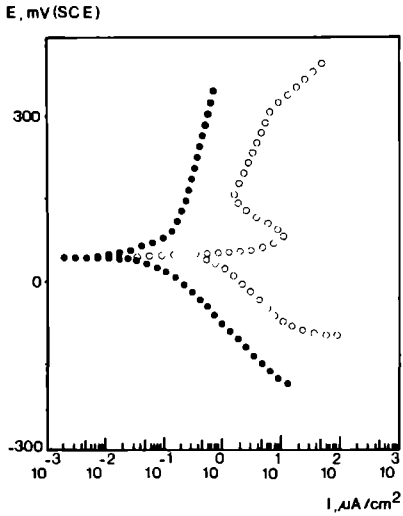

Fig. 3-1 Tafel slopes with apparent signs of spontaneous passivation (oo) or active passive transition (●●) in the anodic branch.

Table 3-6 Arithmetic average of OCP and geometric mean of I_{corr} for the distinct significant treatment combinations.

	OCP mV (SCE)		I_{corr} µA/cm²
Factor	M^+	M	$M^+ + M^-$
Alloy	S^{***}	S^{**}	S^{***}
Aur	− 16	+ 32	0.06
CeW	− 17	+ 6	0.34
OrV	− 22	+ 66	0.12
Str	− 57	+ 56	0 09
Tal	−289	−233	0.93
Tri	−244	−149	1 62
WLW	+ 22	+ 68	0.16
O_2	S^{***}	S^-	S^*
+	− 52	− 3	0.33
−	−126	− 4	0.18
pH	S^-	S^{**}	S^{**}
6 7	− 88	+36	0 18
4 6	− 90	− 80	0 34

M^+ :Saliva Orthana®

M^- :Saliva Orthana® without mucin

S' Significance at i level

In table 3-6 the data on the electrochemical parameters are compressed per factor. Because of the M x H interaction found for the OCP, the results are given for Saliva Orthana with and without mucin. Since there were no interactions between the factor mucin and other main effects for I_{corr}, only the average value of I_{corr} is given. Using the Wilcoxon signed rank test no influence of the factors mucin, oxygen and pH or any interactions on the cathodic Tafel slope could be found. The overall mean equals 200 mV/decade approximately. The anodic Tafel slopes could not be used in most of the cases because of apparent signs of spontaneous passivation or early active-passive transition. Fig. 3-1 gives some typical examples of the behaviour detected.

3.4 Discussion and conclusions

Table 3-6 makes it clear that in the presence of mucin generally lower OCP values occur for all alloys, while I_{corr} is not affected. The fact that I_{corr} is not influenced by the presence of mucin, but OCP is affected, implies a passive type of anodic behaviour i.e. a high Tafel slope in the region of the OCP, which is not affected by the presence of mucin and a cathodic Tafel slope which must shift to lower current densities in the presence of mucin. This behaviour is typical for a so-called cathodic inhibitor (West, 1970). The overall mean cathodic Tafel slope of approximately 200 mV/decade in both SO and P is quite high compared to an approximation of the average slope of 120 mV/decade used by Fontana (1986) This might be

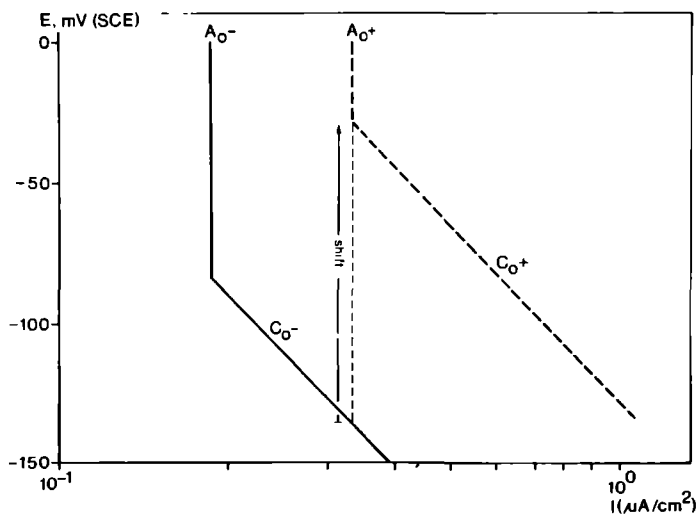

Fig. 3-2 Schematic representation of the cathodic (C) and anodic (A) branches of the polarization curve, consistent with the I_{corr} and cathodic Tafel slope values as observed in case of aerated (O^+) versus deaerated (O^-) artificial saliva.

explained by adsorption inhibition by one of the other components of the artificial saliva used, e.g. benzoate (West, 1970).
Fig 3-2 shows the schematic anodic and cathodic branches, consistent with the measurements in the presence and absence of oxygen in the artificial saliva. It is evident that upon aeration, the cathodic branch shifts to higher potential values. From fig. 3-2 it can be determined that this shift equals approximately 100 mV.
In fig. 3-3 the influence of mucin on the anodic and cathodic behaviour for different levels of pH is schematized. Mucin hardly influences the OCP at pH = 4.6. However, it appears to act as a cathodic inhibitor at pH = 6.7. This experimental observation is the source of the M x H interaction. Cathodic inhibitors appear to be effective in substantially isolating the alloy's surface by a stable surface film (West, 1970). At pH = 4.6, the adsorbed film is evidently unstable. This is consistent with the observation that under clinical conditions a continuous and stable biofilm does not exist at a pH lower than 5 (Glantz, 1988).

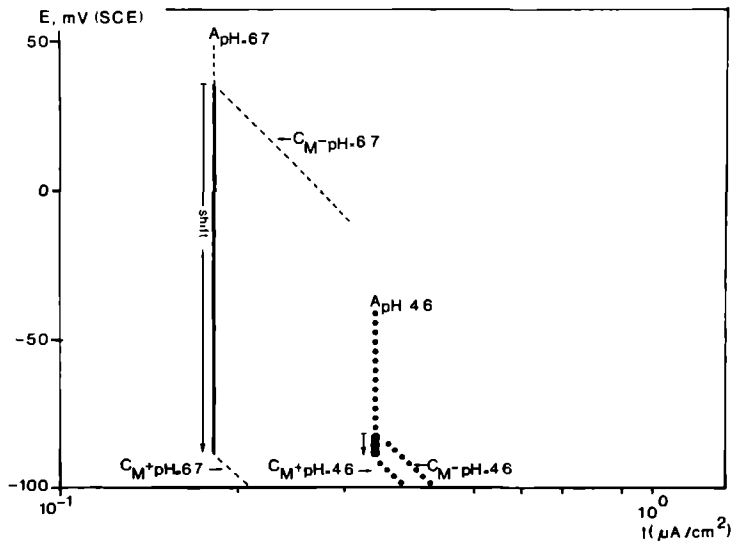

Fig. 3-3 Schematic representation of the cathodic (C) and anodic (A) branches of the polarization curve consistent with the I_{corr} and cathodic tafel slope values as observed in mucin containing (M^+) and mucin free (M^-) artificial saliva at pH = 6.7 and pH = 4.6.

Because most of the alloys investigated are passivating or have a high Tafel slope near the OCP, the presence of mucin does not affect I_{corr}, which is the singularly most important electrochemical parameter related to ion release. This suggests that from the standpoint of corrosion testing its ommission from the artificial saliva is acceptable.

Acknowledgement

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CHAPTER 4

Metallurgical aspects and corrosion behaviour of yellow low-gold alloys*

P.R. Mezger
A.L.H. Stols
M.M.A. Vrijhoef
E.H. Greener

Abstract

Three copper-free type III yellow low-gold alloys (Ag-Au-In-Pd-Zn) were investigated. Microstructural analysis was performed with X-ray diffraction, light microscopy and an electron X-ray microanalysis. The electrochemical behaviour of the alloys was tested with standard potentiodynamic techniques in 0.9% saline solution and an artificial saliva and compared to a traditional high-gold alloy.
The three alloys turned out to be two-phase mixtures of a fcc (matrix) and a bcc (island) phase. The yellow colour, present in spite of the low-gold content, was caused by the disordered PdIn-type, island structure. An additional third structure was seen after etching. However, no distinct phase could be correlated with it. The corrosion behaviour for the experimental alloys, based on cyclic polarization can be considered acceptable in both electrolytes used, but is inferior to the control alloy.

4.1 Introduction

Since the early 1970's the price of traditional high-gold type I-IV casting alloys has increased markedly. This appears to have been the driving force for the introduction of an overwhelming number of so-called alternative systems, including low-gold alloys. One drawback of copper-free low-gold alloys with a gold content lower than approximately 40 wt% is that they are not yellow, but 'white systems'. Recently, copper-free type III alternative alloys containing approximately 20 wt% Au have been introduced, which were probably derived from two Japanese patents of Nippon Shiken Kogyo (1983, 1984). Although variations occur, all alloys are characterized by a chemical composition of about 20 wt% Au, 20 wt% Pd, 40 wt% Ag, 16 wt% In and 4 wt% of Zn.

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* Submitted for publication in Dental Materials

It was the aim of this investigation to assess metallurgical aspects of three selected alloys of this type and to compare their corrosion behaviour to that of a traditional high-gold ADA type III casting alloy.

4.2 Materials and methods

Disc-like specimens (15 mm in diameter x 2 mm) of the 4 casting alloys were made according to the manufacturer's instructions. The specimen size was chosen to represent an upper limit to the clinical thickness requirement of the occlusal aspect and consequently would represent a limiting situation for transport processes depending on cooling rates The brandnames of the respective alloys as well as their chemical composition are given in the tables 4-1 and 4-2. In order to simulate general practice conditions all specimens were cast in a commercial dental laboratory. In all cases, the surface of the three experimental alloys contained some porosities

Table 4-1 The alloys used in this study.

Alloy	Manufacturer	Code designation
Strator3	Cendres et Métaux SA, Bienne, Switzerland	#1
Mirafort 3L	Elephant Edelmetaal BV, Hoorn, the Netherlands	#2
Geco 84	Wieland Edelmetalle GmbH, Pforzheim, FRG	#3
Degulor C	Degussa AG, Frankfurt, FRG	#4

Table 4-2 Chemical composition (wt%) of the alloys used in the unetched condition as determined by electron probe X-ray microanalysis. Standard deviations are given between brackets.

Alloy	Pt	Au	Ag	Pd	Cu	In	Zn	Other
#1		20 0 (0 4)	36 8 (0 5)	21 2 (0 6)		17 7 (0 8)	4 1 (0 3)	Co, Fe, Ru
#2		19 8 (0 7)	36 0 (0 6)	21 9 (0 7)		18 0 (0 4)	3 9 (0 5)	Cu, Co, Ni, Cr
#3		20 2 (0 4)	45 4 (0 3)	13 7 (0 6)		15 7 (0 4)	4 7 (0 6)	Co, Fe, Ni
#4	2 3 (0 5)	74 6 (0 4)	13 4 (0 2)	1 5 (0 3)	7 3 (0 3)		0 7 (0 3)	Fe, Ni

Specimens were routinely screened under a light microscope (Carl Zeiss, Oberkochen, FRG). X-ray diffraction patterns were obtained using a X-ray diffractometer with a stabilized generator (Philips, Eindhoven, the Netherlands) using Cu K_α-radiation and a Ni-filter.

A Camebax electron microprobe type MBI (Cameca, Paris, France), coupled to a TN2000 X-ray analysis system (Tracor Northern, Middleton, Wisconsin, USA) was used for microstructural and quantitative X-ray microanalysis (accelerating voltage 20 kV; stabilized beam current 3.8 nA; take off angle 40°; acquisition 1 minute live time). Specimens were examined in a polished condition and after etching for 20 seconds in aqua regia. The results were based on at least 5 measurements per structure. A linear least-squares fit program was used to obtain net elemental peak intensities and a ZAF correction for bulk specimens was executed. Pure elemental standards were used as references. Etching had only a negligible influence on the chemical composition. Therefore, the microchemical compositions are expected to be unbiased.

Specimens were ground through 800-grit silicon carbide paper under running tap water and subsequently polished through a 1/4-μm alumina paste prior to being immersed into the corrosion cell. Cleaning after polishing was performed ultrasonically in acetone for two minutes (organic debris removal), followed by an ultrasonic treatment for five minutes in distilled water. A standard specimen-holder (K0105, EG & G, Princeton, USA), exposing 1 cm^2 of polished surface, was employed in conjunction with a standard corrosion cell (ASTM Specification G5-69). A saturated calomel (SCE) electrode (K0105, EG & G, Princeton, USA) including a salt bridge, was used as a reference electrode. The counter-electrode consisted of two symmetrically placed carbon rods.

Testing was carried out in 2 electrolytes: a 0.9% saline solution (pH = 5.5) and an artificial saliva (pH = 5.3) according to Meyer and Nally (1975). All tests were run at an ambient temperature of 23 °C. Both solutions were unstirred (stagnant) and were exposed to atmospheric air prior to and during the test. The oxygen content was approximately 7 mg/l (Z800 Oxygen meter, Consort Co, Turnhout, Belgium).

All measurements were performed with a potentiostat/galvanostat (model 273, EG & G, Princeton, USA) connected to an Apple IIE computer. A dedicated software package (Softcorr, EG & G, Princeton, USA) provided facilities to run the tests automatically and evaluate the results obtained.

Testing procedures for each specimen consisted of two polarization runs, interrupted by re-polishing. During the first sequence, the open circuit potential (OCP) was monitored as a function of time for at least one hour. This part of the test was continued until there was no detectable change in OCP for at least two minutes. Subsequently, a potential scan was done from −20 mV (SCE) to +20 mV (SCE) around OCP at a scan rate of 0.1 mV/sec to obtain data for a polarization resistance calculation. It was followed by a potential scan from −250 mV (SCE) to +250 mV (SCE) around OCP at a scan rate of 0.2 mV/sec to provide data for a Tafel-constant calculation. After the re-polishing procedure, a second sequence produced a potentiodynamic hysteresis profile from −1000 mV (SCE) to +1000 mV (SCE) at a scan rate of 0.5 mV/sec. Before this test, the sample was held at

−1000 mV (SCE) for 10 minutes to remove surface oxide films. Scan rates were chosen to be of the same order as those recommended by ASTM and yet allow for the convenient collection of the data. These scan rates were consistent with those used previously by the authors (Vrijhoef *et al.*, 1987).
Generally, I_{corr} values were computed by means of the dedicated software package (Softcorr, EG & G, Princeton, USA). A traditional graphical extrapolation method (Scully, 1981) was used in those cases where the software algorithm could not be employed e.g., because of spontaneous passivation. In this case, the cathodic Tafel-line was extrapolated to the zero current potential (ZCP), i.e. E (I = 0). At least triplicate measurements were done for each alloy. Comparison of corrosion parameters was done statistically utilizing ANOVA and Least Significant Differences (LSD) post hoc intercomparisons.

4.3 Results and discussion

4.3.1 Microstructure

The results of the X-ray diffraction measurements are given in table 4-3. All three low-gold alloys could be indexed on the basis of a two-phase mixture of a fcc phase with a lattice parameter of 0.41 nm and a disordered bcc phase with a lattice parameter of 0.32 nm.
A typical optical photomicrograph representative of all three alloys is shown in fig. 4-1. Based on the relative intensities of X-ray diffraction peaks, the fcc phase is represented by the matrix A, while the bcc phase corresponds with the islands B in fig. 4-1. The matrix phase makes a pale yellow impression. This is consistent with the low-gold content in the order of 30 wt%. The island structure consisting mainly of the disordered PdIn type of intermetallic compound is responsible for

Table 4-3 The lattice characteristics of the phases as detected with X-ray diffraction data. Standard deviations are given between brackets.

Main phase			Second phase	
Alloy	Type	Parameter (nm)	Type	Parameter (nm)
#1	FCC	0 4101 (0 0007)	BCC	0 3202 (0 0004)
#2	FCC	0.4094 (0 0002)	BCC	0 31968 (0 00007)
#3	FCC	0 4087 (0 0003)	BCC	0 3186 (0 0005)

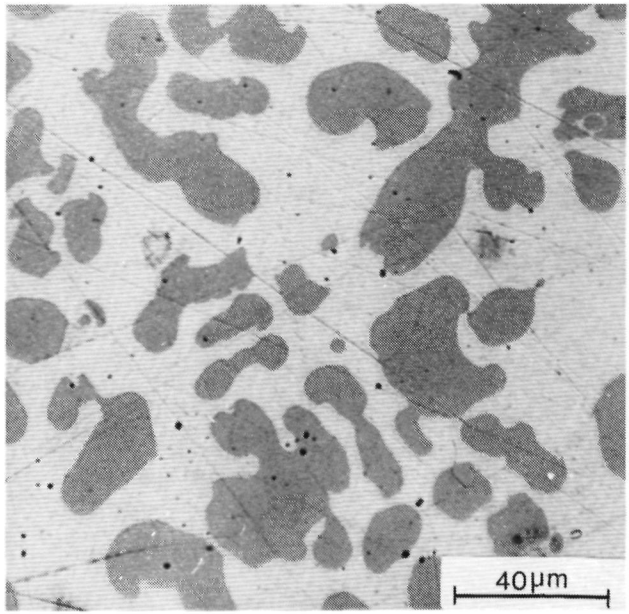


Fig. 4-1 Light optical micrograph of #2 (525x) in the unetched condition.

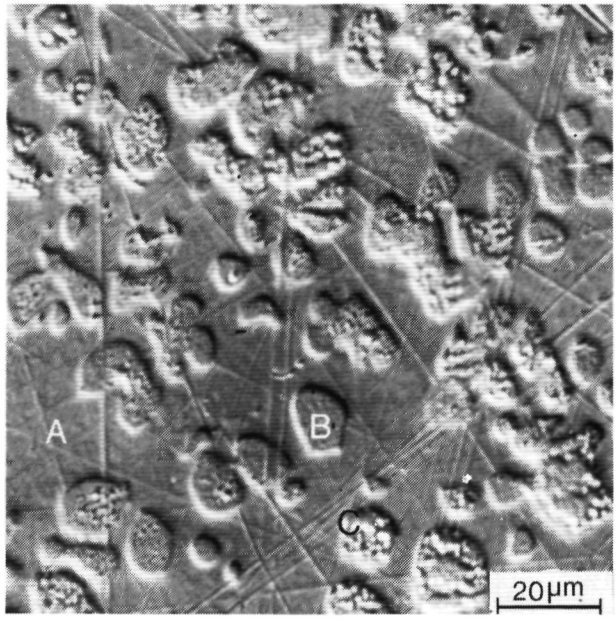


Fig. 4-2 Secondary electron image of#1 (670x) in the etched condition. A, B and C are defined in table 4-4.

Table 4-4 Chemical composition (wt%) of the low-gold alloy structures (A,B and C) in the etched condition as determined by electron probe X-ray microanalysis. Standard deviations are given between brackets.

Alloy	Au	Ag	Pd	In	Zn	Other
#1 A	31.7	58 2	4 8	3.0	1 6	Cu, Co, Ga
	(1.2)	(1.3)	(0 4)	(0 5)	(0.3)	
B	10.9	12.2	40 6	30.2	6.0	Cu, Co, Fe
	(1 5)	(0 2)	(1 3)	(0 6)	(0.2)	
C	12.7	28	32	22 9	4.5	Cu, Fe
	(1.0)	(4)	(3)	(1.7)	(0.7)	
#2 A	30	59	5.4	3 9	1 5	Pt, Cu, Co,
	(4)	(4)	(0.1)	(0.7)	(0.3)	Fe, Ni, Sn
B	17	24	32	22	4.2	Pt, Co, Fe,
	(2)	(5)	(4)	(3)	(0 7)	Ni
C	27	58	9	4		Cu, Co, Fe,
	(7)	(10)	(3)	(2)		Ni, Si, Zn
#3 A	28 6	56.7	3.3	8.3	2.4	Cu, Co, Fe,
	(1.7)	(1.5)	(0.6)	(1.9)	(0 9)	Ga, Sn
B	7 3	11.1	39.4	32.9	8 7	Pt, Cu, Co,
	(1.8)	(0.9)	(1.4)	(0.9)	(0.8)	Fe, Ni, Ga
C	33	48	12	4	1 7	Cu, Sn, Ga
	(4)	(3)	(4)	(3)	(0 6)	

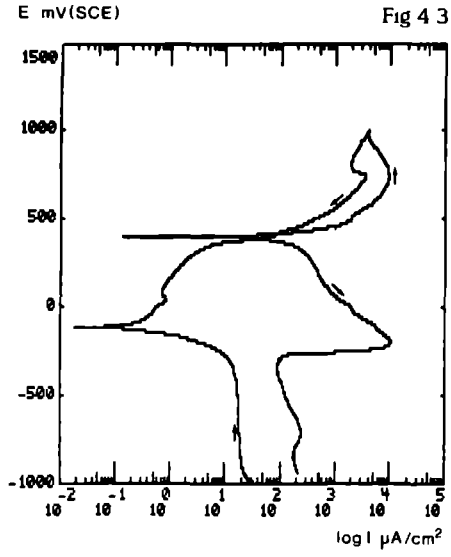
the yellow gold-like appearance of these alloys (Iljuschenko *et al.*, 1984). Table 4-3 makes it clear that phase A is essentially a Ag-Au solid solution with minor additions of Pd, In and Zn. Structure B is a Pd-In phase with substantial additions of Au, Ag and Zn. The lattice parameter of B is in agreement with that of the PdIn (Pm3m) structure (Pearson, 1964), although phase B is a disordered one. This is in agreement with the X-ray results in table 4-3 because the electron/atom ratio of the bcc structure in the three alloys investigated were 1.26, 1.17 and 1.36 respectively, which is in the range of stability of both the stable bcc structure (Hume-Rothery and Raynor, 1962) and that of the binary PdIn intermetallic compound (Hansen, 1958).

To reveal the microstructure further, the alloys were etched in aqua regia, whereupon a third structure (C) was detected in the three alloys (#1,2; fig. 4-2). Table 4-4 contains also the chemical composition of C as determined by electron probe X-ray microanalysis. The fact that no evidence of the C phase was obtained by X-ray diffraction may be explained on the basis of its low volume percentage.

4.3.2 Corrosion

Typical examples of a cyclic polarization diagram of the three low-gold alloys and the control alloy in both electrolytes are shown in the figs. 4-3 to 4-6. The means and standard deviations of experimentally determined values for OCP, ZCP and I_{corr} are given in table 4-5 for 0.9% saline solution and the artificial saliva. Because of the large standard deviations associated with this type of measurement, main effects are seen only between alloy and I_{corr} with $p < 0.1$ for 0.9% saline solution and $p < 0.05$ for artificial saliva. LSD post hoc analysis reveals significant difference ($p \leq 0.05$ between alloy #2 and the remaining alloys). From the table of mean values it can be computed that I_{corr} for alloy #2 is about 3 times larger than the group mean.
Cyclic polarization in artificial saliva disclosed a peak in the cathodic part of the forward scan at about −500 mV (SCE), which was not found in 0.9% saline solution. Some anodic current density values, as derived from the cyclic polarization diagrams, are given in table 4-6.
For the experimental alloys, a distinct decrease in the slope of the potentiodynamic scan in the forward direction (anodic Tafel slope) occurred in both 0.9% saline solution (300-350 mV vs SCE) and in artificial saliva (320-400 mV vs SCE) indicative of increasing corrosion rate (figs. 4-3, 4-4). For the experimental alloys this rate then decreased between +700 and +800 mV (SCE), resulting in a current density peak. For alloy #2 in artificial saliva the current density increased up to scan reversal. In the anodic part of the reverse scan current densities were lower. In 0.9% saline solution a small current density peak occurred between +750 and +690 mV (SCE), corresponding with the peak in the forward scan. In both solutions in the cathodic part of the reverse scan a substantial current density peak occurred between −145 and −245 mV (SCE).
For the control alloy, current densities as derived from the cyclic polarization diagram were extremely low up to values above +750 mV (SCE) in 0.9% saline solution and +850 mV (SCE) in the artificial saliva. Current densities in the anodic part of the reverse scan were lower than in the corresponding forward scan. A peak in the cathodic part of the reverse scan occurred from 0 to −100 mV (SCE).

The ZCP values found in each electrolyte were 180 to 240 mV lower than the corresponding OCP for the alloys investigated. This discrepancy may be related to signs of spontaneous passivation at the surface of the alloys in terms of a film formed after polishing or upon immersion. Table 4 makes it clear that structure A essentially has the same composition for all experimental alloys. The chemical composition of structure B is essentially the same for the alloys #1 and #3, while B contains considerably more Ag in place of Pd and In in alloy #2. This might indicate the composition of B to be of importance to the relatively high I_{corr} value of #2 in both electrolytes. This is unfavourable as it is an indication of its electrochemical activity under isolated conditions.
The cathodic peak in the forward part of the polarization scan around −500 mV (SCE), present for all alloys tested, seems to be related to one of the components of the saliva substitute, because it did not appear in 0.9% saline solution.



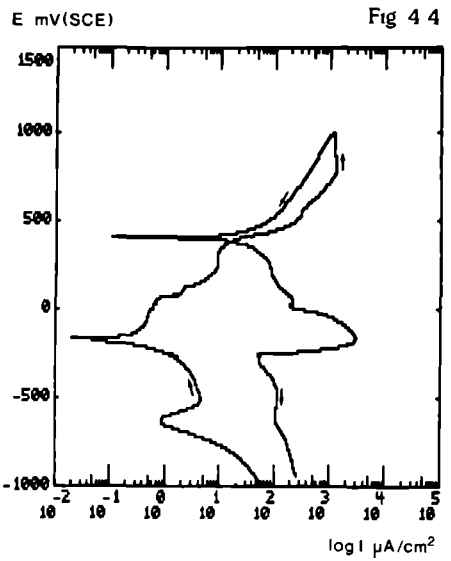
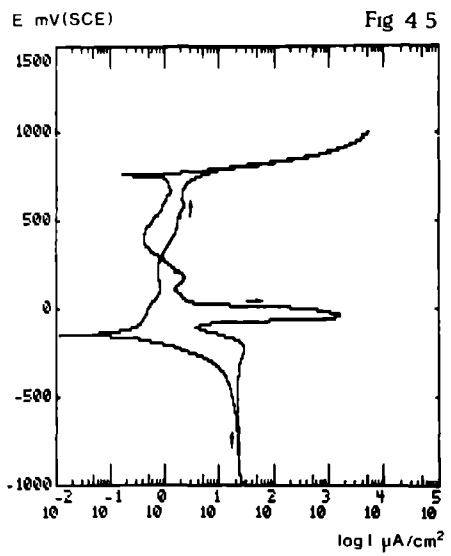


Fig 4-3 A typical cyclic polarization diagram of a low-gold dental alloy (#1) in 0 9% saline solution

Fig 4-4 A typical cyclic polarization diagram of a low-gold dental alloy (#1) in artificial saliva



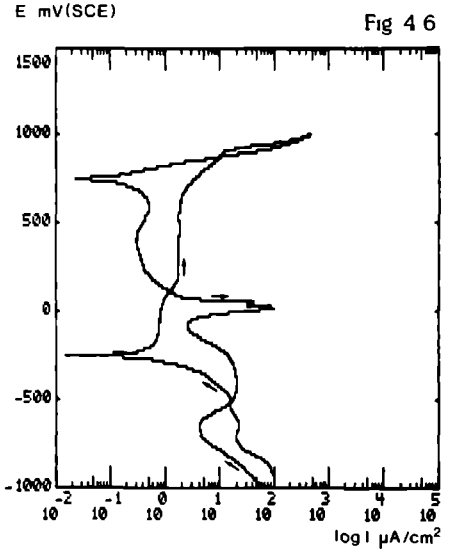


Fig 4-5 A typical cyclic polarization diagram of the control alloy (#4) in 0 9% saline solution

Fig 4-6 A typical cyclic polarization diagram of the control alloy (#4) in artificial saliva

Table 4-5 OCP (mV vs SCE), ZCP (mV vs SCE) I_{corr} ($\mu A/cm^2$) of the alloys #1 to #4 in 0.9% saline solution and an artificial saliva. Standard deviations are given between brackets.

	0 9% Saline solution			Artificial saliva		
Alloy	OCP	ZCP	I_{corr}	OCP	ZCP	I_{corr}
#1	41 (83)	−142 (50)	0 08 (0 10)	1 (83)	−352 (128)	0 14 (0 14)
#2	21 (38)	−190 (39)	0 52 (0 46)	8 (36)	−339 (180)	0 97 (0 31)
#3	−37 (40)	−170 (32)	0 04 (0 03)	−85 (70)	−220 (85)	0 32 (0 27)
#4	80 (54)	−140 (50)	0 02 (0 01)	3 (128)	−143 (100)	0 04 (0 03)

Table 4-6 Mean current density values in ($\mu A/cm^2$) at different potentials (mV vs SCE) derived from the cyclic polarization diagram of the three (yellow low-gold) alloys in 0 9% saline solution and an artificial saliva Relative accuracy of the respective determinations ± 50%

0.9% Saline solution

	Potential				
Alloy	+ 100	+ 200	+ 300	+ 400	+ 500
#1	2 1	1 8	3 0	52	2270
#2	2 8	5 6	7 1	201	1720
#3	2 0	6 2	13	3590	5460
#4	1 1	1 3	1 2	1 3	2 0

Artificial saliva

	Potential				
Alloy	+ 100	+ 200	+ 300	+ 400	+ 500
#1	4 6	6 0	7 6	23	248
#2	7 0	9 6	9 8	37	319
#3	1 3	2 0	4 4	45	675
#4	2 3	2 2	2 0	1 7	2 0

The corrosion behaviour of the four alloys, was characterized by low current densities in both electrolytes up to slightly over +300 mV (SCE), the anodic limit the area of oral interest (Ewers and Greener, 1985; Corso *et al.*, 1985). Thus corrosion resistance of the alloys investigated may be expected to be sufficient for the normal physiologic electrochemical excursions. Anodic polarization beyond the region of +320 to +350 mV (SCE) resulted in a relatively large current density increase for the alloys #1, 2 and 3 in 0.9% saline solution compared to the artificial saliva (fig. 4-6). This may be attributed to both the differences in Cl^- content and to protective components of the artificial saliva such as the phosphate. The control alloy has a substantial additional anodic safety-zone under extreme conditions in both electrolytes. The lower current densities after scan reversal indicate that the alloys investigated do not show any pitting tendency. The casting porosities of alloy #1, 2 and 3 obviously did not affect alloy behaviour. In the reverse scan the cathodic peak being present ranging from −145 to −245 mV (SCE) for the experimental alloys appears to be related to reduction of the film formed in the anodic part of the polarization scan. For the control alloy the cathodic peak during the reverse scan is evident in the range from 0 to −100 mV (SCE). Such peaks reportedly (Wright *et al.*, 1981) are correlated to Ag reduction.

4.4 Conclusions

It might be concluded that the three yellow low-gold alloys have a fcc matrix mainly consisting of Ag, Au with minor additions of Pd, In and Zn and an island structure of the disordered PdIn type. The alloys also showed indications of a third structure which could not be resolved in the X-ray diffraction. The yellow colour of the alloys is mainly due to the disordered PdIn phase. For all alloys, cyclic polarization testing indicated sufficient corrosion resistance for normal physiologic electrochemical excursions. However, because of probable lower nobility of the second phase, the corrosion current density of #2 is less desirable in that an I_{corr} of about 3 times that of alloy #1 and #3 is seen.

Acknowledgement

We are indebted to mrs. A.F.M. Leydekkers-Govers for carrying out part of the experiments.

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CHAPTER 5

Palladium-silver alloys (PART 1)

Metallurgical aspects of palladium-silver porcelain-bonding alloys*

P.R. Mezger
A.L.H. Stols
M.M.A. Vrijhoef
E.H. Greener

Abstract

Metallurgical aspects of five commercial Pd-Ag porcelain-bonding alloys have been investigated using X-ray diffraction, light microscopy and X-ray microanalysis.
All alloys are mainly single-phase systems, but they appear to be inhomogeneous due to constitutional supercooling.
Porcelain-firing times are presumably insufficient to reach homogeneity. Two alloys show a virtually identical chemical composition, but a differing amount of segregation which should be attributed to minor components controlling the solid diffusion process.
Both indium-containing alloys show signs of a minor second phase which could not be identified due to its finely dispersed character.

5.1.1 Introduction

A variety of alternative porcelain-fused-to-metal (PFM) alloys has been introduced on the dental market during the past two decades. Among these alternative alloys the palladium-silver alloy system has gained early popularity because of favourable handling characteristics (Van der Zel, 1982; Hohmann, 1985). The major problem associated with this system, namely the discoloration of the porcelain veneer, can be virtually avoided now (Van der Zel, 1982; Hohmann, 1985; Reel *et al.*, 1986; Ringle *et al.*, 1986) by the use of special porcelains or intermediate opaque layers.

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* Accepted for publication in the Journal of Dentistry

Although Pd-Ag type of alloys have gained in popularity, information as to the microstructure of these systems is scarce (Bessing and Bergman, 1986; Payan *et al.*, 1986).
It was the aim of this study to investigate the microstructural aspects of some commercial Pd-Ag alloys.

5.1.2 Materials and methods

Disc-like specimens (15 mm diameter x 2 mm) of the 5 alloys used (table 5.1-1) were made according to the instructions of the manufacturers. The specimen size was chosen to represent an upper limit to the clinical thickness requirement of the occlusal aspect with the understanding, that it would represent a limiting situation for transport processes depending on cooling rate. In order to simulate general practice conditions, all specimens were cast by a commercial dental laboratory using the manufacturers' instructions. All alloys used received a simulated porcelain-firing heat treatment (F), consisting of an oxidation treatment, one opaque and two gingival porcelain-firings under vacuum as well as a glazing procedure at ambient air pressure. Time and temperature for each of these procedures are specific for each alloy-porcelain combination. Moreover, alloy A was additionally tested in the as cast condition (AC) as an example of an alloy used as a type IV alloy substitute. In this case the alloy generally is used in the as cast condition.

Table 5.1-1 The Pd-Ag alloys used in this investigation.

Alloy	Code	Manufacturer
A 35	(A)	Austenal Dental, Köln, FRG
Estheticor Actual	(E)	Cendres et Métaux SA, Bienne, Switzerland
Ceram W-1	(C)	Williams gold, Buffalo, USA
Orion Virgo	(O)	Elephant, Hoorn, the Netherlands
Pors-on 4	(P)	Degussa, Frankfurt, FRG

Specimens of the alloys involved were routinely screened under a light microscope (Carl Zeiss, Oberkochen, FRG). X-ray diffraction patterns were obtained using an X-ray diffractometer with a stabilized generator (Phillips, Eindhoven, the Netherlands) using Cu K_α -radiation and a Ni-filter.
A Camebax electron microprobe type MB1 (Cameca, Paris, France), coupled to an X-ray analysis equipment (Tracor Northern, Middleton, Wi, USA), was used for microstructural and quantitative microchemical analysis (accelerating voltage 20 kV; stabilized beam current 3.8 nA, take-off angle 40°, acquisition 1 minute live time). Specimens were examined in a highly polished condition and after etching

in Aqua Regia for 20 seconds. The results were based on at least 5 measurements per structure. A linear least-squares fit program was used to obtain net elemental peak intensities and a ZAF correction for bulk specimens was executed. Pure elements were used as standards. Etching only had a negligible influence on the chemical composition. Therefore, the microchemical compositions are expected to be unbiased.

5.1.3 Results

The results of the X-ray diffraction measurements are given in table 5.1-2. All alloys could be indexed as single-phase fcc with a lattice parameter of ca. 0.396-0.398 nm. Additional peaks which could not be indexed, were seen in alloy O and P. The overall chemical composition of the distinct alloys, as determined by electron microprobe, are given in table 5.1-3. The chemical composition of the different alloy structures in the etched condition are given in table 5.1-4.
Light microscopy of the Pd-Ag alloys revealed a dendritic structure for alloy A in the as cast (fig. 5.1-1) and fired condition and alloy C as fired. The other alloys showed distinct etching of grain boundaries with less indication of dentritic solidification (fig. 5.1-2). Electron micrographs of these alloys show a smooth (fig. 5.1-3:a) and a rougher structure (fig. 5.1-3:b) with compositions as detailed in table 5.1-4.
The alloys O and P in the fired condition showed a more heavily segregated structure than those of A (AC and F) and C (F) (table 5.1-4). In these alloys the 'b' structure is enriched in Ag with a relatively low Pd content. The Sn content appears to be homogeneously distributed. In case of alloy E (as fired) a and b appear to be identical.

Tabel 5.1-2 The lattice characteristics of the phas(e) of the Pd-Ag alloys detected with X-ray diffraction. Standard deviations are given between brackets.

		Lattice characteristics		
Alloy	Condition	Type	Parameter (nm)	Other phase(s)
A	AC	FCC	0.3964 (0.0007)	
A	F	FCC	0.3979 (0.0006)	
C	F	FCC	0 3977 (0 0006)	
E	F	FCC	0.3976 (0.0002)	
O	F	FCC	0.3979 (0 0004)	+
P	F	FCC	0.3973 (0 0003)	+

FCC Face-centered cubic
AC . As cast
F · As fired
\+ Indication of additional phases

Table 5.1-3 Chemical composition (wt%) of the Pd-Ag alloys as determined by electron probe X-ray microanalysis. Estimated standard deviations are given between brackets.

Alloy	Condition	Ag	Pd	In	Sn	Zn	Other
A	AC	28.0 (0.8)	58.6 (0.9)		12.8 (0.5)		Cu, Ga, Co
A	F	28.1 (0.8)	57.9 (0.9)		12.4 (0.6)		Cu, Co, Fe, Ga, In, Zn, Ru
C	F	36.7 (0.6)	52.5 (0.7)		10.2 (0.4)		Pt, Co, Fe, In, Ga
E	F	37.1 (0.2)	52.2 (0.4)		10.3 (0.4)		Co, Fe, In, Ru
O	F	27.7 (0.7)	58.0 (0.5)	6.9 (0.4)	6.2 (0.5)		Pt, Cu, Co, Fe, Ga, Zn
P	F	28.2 (0.4)	58.4 (1.6)	4.5 (0.2)	6.7 (1.1)	1.6 (0.5)	Pt, Cu, Co, Fe, Ga, Ru

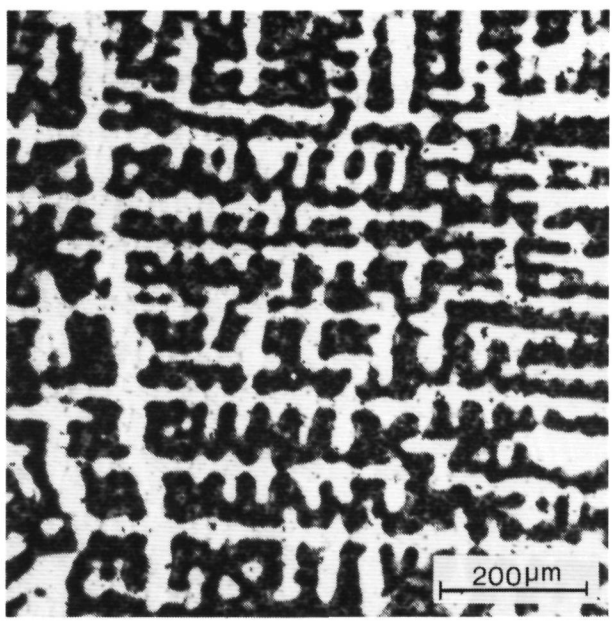

Fig. 5.1-1 Light optical micrograph of alloy A 35 as cast (100x) in the etched condition.

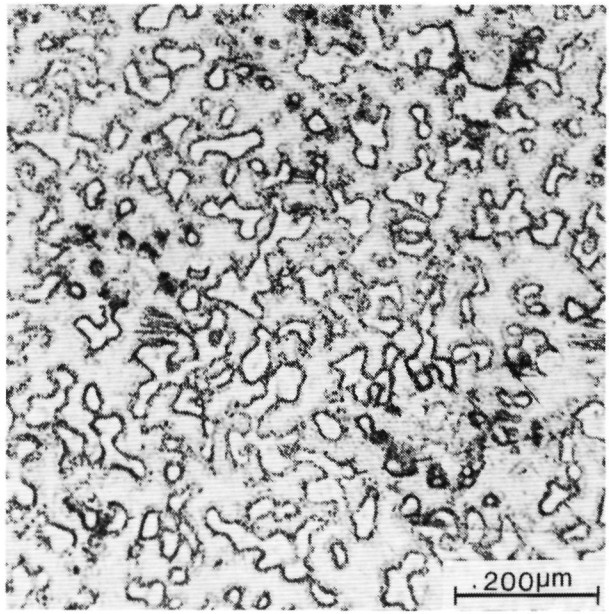

Fig. 5.1-2 Light optical micrograph of alloy Estheticor Actual as fired (100x) in the etched condition.

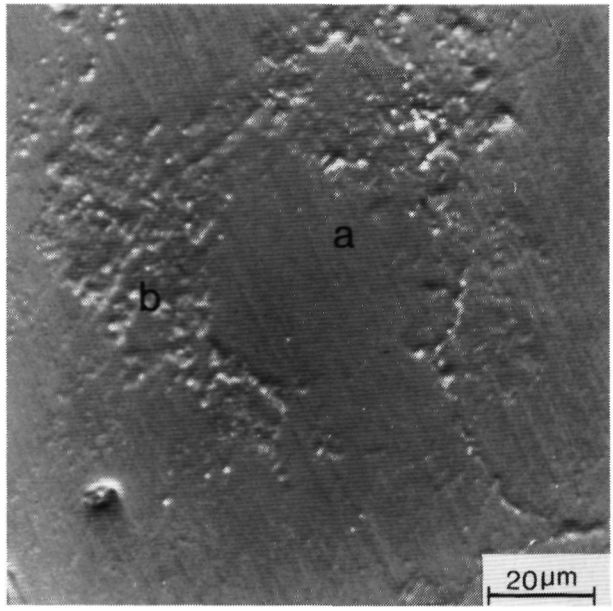

Fig. 5.1-3 Secondary electron image of alloy Pors-on 4 as fired (670x) in the etched condition. Structures a and b are defined in table 5.1-4.

Table 5 1-4 Chemical composition (wt%) of the different structures of the Pd-Ag alloys in the etched condition as determined by electron probe X-ray micro-analysis. Estimated standard deviations are given between brackets

Alloy	Condition	Structure	Pt	Ag	Pd	In	Sn	Zn	Other
A	AC	a		24 2	61 4		13 5		Pt, Cu, In,
				(0 6)	(1 2)		(0 6)		Fe
		b		36	51		11 8		Pt, Cu, Co,
				(2)	(2)		(08)		Fe, Ga, Ru
A	F	a		24 4	61 3		13 7		Cu, Co
				(1 4)	(1 2)		(0 5)		
		b		32	54		12 7		Cu, Co, Fe,
				(4)	(3)		(0 9)		Ga, In, Zn
C	F	a		35	54		10 4		Pt, Cu, In,
				(4)	(4)		(0 7)		Fe, Ru,
		b		43 5	46 2		9 8		Cu, Co, In,
				(1 6)	(0 8)		(0 6)		Zn, Ru
E	F	a		37	51		10 0		Fe, In, Ga,
				(5)	(4)		(1 0)		Ru
		b		37	52		10 9		Cu, Fe, In,
				(3)	(3)		(0 4)		Ga, Ru
O	F	a	0 8	25	60	7 4	6 1		Cu, Fe, Zn
			(0 1)	(4)	(4)	(0 8)	(0 4)		
		b		41	47	4,8	5,8		Pt, Cu, Co,
				(6)	(5)	(1,1)	(1,1)		Fe
P	F	a		27	60	4 8	6 6		Pt, Cu, Co,
				(5)	(3)	(0 6)	(0 9)		Fe, Ga, Zn
		b		41	48	3 3	5 6	1 2	Cu, Fe
				(6)	(5)	(1 1)	(0 8)	(0 5)	

5.1.4 Discussion

Although the ϵ_γ are mainly single-phase systems, all alloys investigated appear to be inhomogeneous in nature due to constitutional supercooling. In the case of alloy A (as cast) the difference in composition of Ag and Pd between the structures a and b is 10 wt% approximately, which is of the order of the width of the distance between solidus and liquidus in the Ag-Pd binary (Hansen, 1958). Upon firing only 2 wt% of the difference is recoverable. All the remaining alloys except for E showed similar differences in Ag and Pd concentration after firing. Apparently for these alloys the porcelain-firing cycle is insufficient to remove compositional differences produced by solidification during casting. Payan *et al.* (1986) reported a

homogeneous single phase structure for a Pd (59.3 wt%)- Ag (29.6 wt%)- Sn (8.8 wt%)- In (2.2 wt%) alloy after heat treatment at 1000°C for 2 hours. Porcelain-firing times for the alloys investigated here, are in the order of a factor five times shorter, which might explain for their remmant inhomogeneity. The Pd-Ag-Sn alloys (A, C and E) appear to be more homogeneous than the Pd-Ag-Sn-In alloys (O and P), in that Pd and Ag concentration differences are larger and an indeterminate second phase was seen in the latter. This is most presumably related to the addition of In in the latter systems. For alloys A, C, O and P, the Ag concentration is enriched and the Pd concentration is diminished in structure b compared to structure a. In alloy E no compositional difference between a and b exists. The difference between C and E is striking in that, while both alloys have virtually the same chemical composition, alloy C is much more segregated than alloy E. Apparently, minor components can play an important role controlling the solid diffusion process.

Because the unknown phase in O and P is only a minor one, it is not easily detected by means of light microscopy or electron microprobe analysis. This may occur in case the phase is finely dispersed in the matrix.

No information is available as to whether the inhomogeneous structure of some of the systems gives rise to increased corrosion. Further research will concern this aspect.

Acknowledgement

The authors are endebted to mrs. A.F.M. Leydekkers-Govers for carrying out part of the experiments.

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CHAPTER 5

Palladium-silver alloys (PART 2)

The corrosion behaviour of palladium-silver ceramic alloys*

P.R. Mezger
M.M.A. Vrijhoef
E.H. Greener

Abstract

Five commercial Pd-Ag alloys were investigated Their electrochemical behaviour was tested with standard potentiodynamic techniques in 0.9% saline solution and an artificial saliva and compared to high-Pd systems.
Corrosion characteristics of the Pd-Ag alloys were quite similar irrespective of microstructural and compositional differences. In the area of oral interest all alloys showed a sufficient corrosion resistance.
The alloys were, unlike their high-Pd counterparts, adversely affected by a high Cl^- content under more extreme conditions and a visible film formed.

5.2.1 Introduction

Among the alternative ceramic casting alloys, the palladium-silver alloy systems have gained early popularity because of favourable handling characteristics (Van der Zel, 1982; Hohmann, 1985). Literature on chemical composition and microstructure have been reviewed and experimental data of commercial Pd-Ag based alloys presented elsewhere (Mezger *et al.*, 1986). Corrosion data on this alloy type, however, are scarce and incomplete (Vaidyanathan and Prasad, 1981; Newman and Greener, 1984; Lane *et al.*, 1985).
It was the aim of the present study to investigate the corrosion behaviour of five commercial palladium-silver alloys.

5.2.2 Materials and methods

The alloys used in this study and their respective chemical composition as determined by electron microprobe analysis are presented in table 5.2-1. Alloy samples

* Accepted for publication in Dental Materials

were tested in the simulated porcelain-fired condition according to manufacturers' instructions. Previously, the authors have shown (Mezger *et al*, 1986) that all alloys are primarily single-phase fcc with a lattice parameter close to that of Pd. The microstructures revealed elemental segregation due to constitutional supercooling In addition two of the alloys (P and O) exhibited a small concentration of an undetermined second phase. Sample preparation, experimental design and details as to the electrochemical measurements, are described by Vrijhoef *et al.* (1987). Utilizing these methods, standard deviations of the open circuit potential (OCP) and zero current potential (ZCP) are found to be 50 and 70 mV respectively. Coefficients of variation of the corrosion current density (I_{corr}) as well as the current density at a particular overvoltage are about 50%.
All alloys were tested in both 0 9% saline solution and an artificial saliva according to Meyer and Nally (1975).

Table 5.2-1 Chemical composition (wt%) of the Pd-Ag alloys as determined by electron probe X-ray microanalysis.

Alloy	Code	Manufacturer	Ag	Pg	In	Sn	Zn	Balance
A 35	(A)	Austenal Dental, FRG	28 1	57 9		12 4		Cu, Co, Fe, Ga, In, Zn, Ru
Ceram W-1	(C)	Williams Gold, USA	36 7	52 5		10 2		Pt, Co, Fe, In, Ga
Estheticor Actual	(E)	Cendres et Métaux SA, Switzerland	37 1	52 2		10 3		Co, Fe, In, Ru
Onon Virgo	(O)	Elephant, the Netherlands	27 7	58 0	6.9	6 2		Pt, Cu, Co, Fe, Ga, Zn
Pors-on 4	(P)	Degussa, FRG	28 2	58 4	4 5	6 7	1 6	Pt, Cu, Co, Fe, Ga, Ru, Si

5.2.3 Results

Corrosion behaviour in terms of respective cyclic polarization diagrams of the five alloys were very similar. Figs. 5.2-1 and 5.2-2 show typical diagrams in each electrolyte. Table 5.2-2 presents the OCP and ZCP of the forward scan as well as the I_{corr} in both 0.9% saline solution and an artificial saliva. Because the Pd-Ag alloys are competitive with the high-Pd systems, the range of values for the latter ones, as presented previously (Mezger *et al.*, 1986), are depicted as well.
In artificial saliva, in the cathodic part of the forward scan, a peak occurred varying

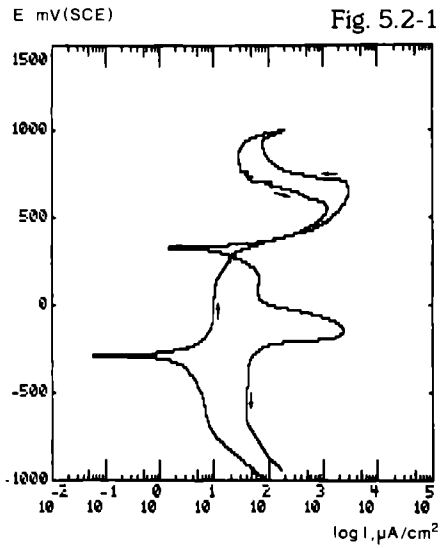

Fig. 5.2-1

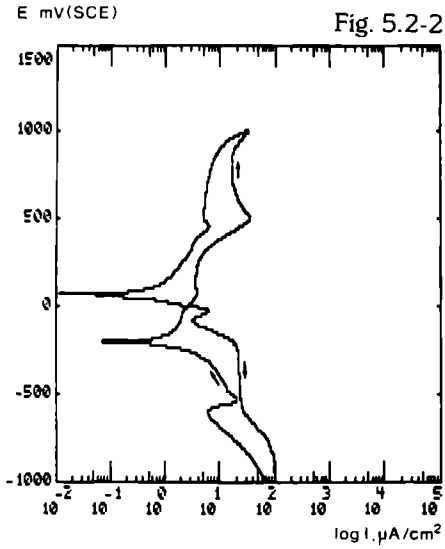

Fig. 5.2-2

Fig. 5.2-1 Cyclic polarization diagram of Ceram W-I in 0.9% saline solution.

Fig. 5.2-2 Cyclic polarization diagram of Ceram W-I in an artificial saliva according to Meyer and Nally (1975).

Table 5.2-2 OCP (mV vs SCE), ZCP (mV vs SCE) and I_{corr} ($\mu a/cm^2$) of the Pd-Ag alloys in 0.9% saline and artificial saliva.

	OCP	ZCP	I_{corr}	OCP	ZCP	I_{corr}
Alloy	0.9% saline			Artificial saliva		
A	+ 30	−180	0.10	+ 60	−130	0.05
C	− 10	−250	0 03*	− 0	−200	0.12
E	− 20	−150	0.03	− 10	−180	0.07
O	− 10	−160	0.04	− 30	−140	0.14
P	+ 90	−140	0.05	+ 30	−150	0 04
High-Pd	− 30/	−230/	0.03/	+ 10/	−230/	0.05/
(range)	+130	−120	0.17	+150	− 80	0.37

* extrapolated

from −530 to −370 mV (SCE). In the anodic part of the forward scan, current density values were < 15 $\mu A/cm^2$ in both electrolytes until approximately +300 mV (SCE). Between +300 and +400 mV (SCE) a distinct current density increase occurred in 0.9% saline solution for all alloys, resulting in a peak ranging from +530 to +610 mV (SCE) with current densities ranging from 1000 to 2500

$\mu A/cm^2$ (table 5.2-3). At still higher potential a current density decrease of 1-2 orders of magnitude occurred. There was evidence for a small second anodic current density increase just before scan reverse. For all alloys in the anodic part of the reverse scan, current density was lower than at similar potential values in the forward scan. A peak was seen in the range from +580 to 460 mV (SCE). The ZCP in the reverse scan was found at higher potential values compared to the forward scan (table 5.2-2). In the cathodic part of the reverse scan a peak occurred in the range from −10 to −150 mV (SCE).
The behaviour of the alloys in artificial saliva was analogous to that in 0.9% saline solution, except that the anodic peak was displaced to lower potentials and the peak current density was two orders of magnitude less. In case of C a tiny anodic peak occurred at +460 mV (SCE). Again, ZCP was situated at higher potential values compared to the forward scan. Some indications of a cathodic peak in the reverse scan occurred at −10 to −30 mV (SCE). After cyclic polarization, alloy samples showed surface discoloration in 0.9% saline solution. In all cases visual inspection of the samples revealed no signs of pitting or crevice corrosion.

Table 5.2-3 Anodic peak potentials (PP), their corresponding current density (PC), along with current density values at +300 mV (SCE) in 0.9% saline solution and an artificial saliva.

	I_{300mV}	PP	PC	I_{300mV}	PP	PC
Alloy	0.9% saline			Artificial saliva		
A	11.8	+570	850	10.9	+510	43
C	6.4	+600	1761	5.0	+500	34
E	4.3	+570	2200	13.9	+440	21
O	6.1	+530	2200	10.2	+480	30
P	2.5	+590	2300	4.5	+500	26
High-Pd	2/	+550/	17/	4/	+520/	24/
(range)	15	+650	230	17	+660	45

5.2.4 Discussion

In general, the ZCP was in the order of 100-300 mV lower than the OCP. This discrepancy may be related to the spontaneous passivation of the alloys, either in terms of a film formed after polishing or upon direct immersion. Cathodic polarization at −1000 mV (SCE) may be expected to reduce some of this film and, thus, subsequently depress the measured corrosion potential.

Given the accuracy of the experiment, the OCP and ZCP of the 5 alloys were essentially the same (table 5.2-2). Similarly, I_{corr}, which gives an indication of the corrosion resistance of a system allowed to function in an isolated position, was equivalent for the alloys in both electrolytes.

In an experiment with binary alloys of Pd and Ag, with compositions changing with 20 wt% in differing saline solutions, Sastri *et al.* (1982) showed that the OCP shifted to the noble direction with Pd alloying. For an alloy composition of 40 wt% Ag and 60 wt% Pd, an OCP value of +390 mV (SCE) was mentioned in a 1% saline solution. For more complex alloy systems, as used in this study, OCP values in 0.9% saline solution were considerably lower. This indicates a depressing influence of Sn on this mixed potential while in case of P and O, indium also may play a role.

The cathodic peak in the forward scan in the range from −530 to −370 mV (SCE) seems to be related to the chloride ion, because it is only present in case of artificial saliva. It may be associated with the Cl^- concentration. An adsorbed chloride layer or a chloride containing film could be involved. A high Cl^- concentration will shift the peak potential to lower values which is consistent with the absence of the peak in 0.9% saline.

It appears that all alloys were immune or passive in both the stagnant aerated saline solution and artificial saliva to at least anodic potentials of +300 mV (SCE). Beyond this potential, which is considered to be an anodic boundary value for the area of oral interest (Corso *et al.*, 1985; Ewers and Greener, 1985), a distinct current density increase occurred in 0.9% saline solution. In artificial saliva this increase is only a slight one. Since the high-Pd alloys are competitors with the Pd-Ag alloys, it is of interest to contrast their corrosion behaviour. The pertinent data for the high-Pd alloys are given at the bottom of the tables 5.2-2 and 5.2-3. It can be seen that the passive/immune regions for the Pd-Ag alloys are up to 100 mV less than those for the high-Pd systems (i.e. a substantial current increase at 300 mV vs 400 mV (SCE)). The ZCP and I_{corr} values appear to be the same for both alloy systems. These findings indicate that under normal conditions the Pd-Ag and high-Pd alloys would be equivalent from a corrosion point of view. However, high-Pd alloys would be more resistant to potential excursions away from normal oral conditions.

As can be seen from table 5.2-3, the peak current density seen in 0.9% saline solution is 1 to 2 orders of magnitude higher than in artificial saliva and the peak potential is in the order of 100 mV higher. The Cl^- ion must then be implicated in the breakdown of whatever passive/immune system exists above 300-400 mV (SCE) in these alloys. Studies on high-Pd alloys indicate that a similar phenomenon does not exist in those materials (Mezger *et al.*, 1986).

Since surface discoloration is seen after cyclic polarization in 0.9% saline solution and a pronounced cathodic peak is evident in the region of −45 to −150 mV (SCE), one may hypothesize the formation of a chloride containing film in aggressive media. This film may be the cause of the repassivation occurring at +500 mV (SCE) or, alternatively, surface enrichment of Pd may occur if the film is soluble. In artificial saliva on the other hand, no visible film is seen and the cathodic peaks at

−10 to −150 mV (SCE) are not pronounced and occur at higher potentials. This is further confirmation of a Cl^- dependent corrosion process. It should also be emphasized that the current density in the reverse scan for both 0.9% saline solution and artificial saliva is lower than that of the anodic part of the forward scan. This indicates that the corrosion processes occurring in the potential region of +300 to +1000 mV (SCE) are not associated with pitting phenomena (Galvele, 1983).
Most presumably, the cathodic peak during the reverse scan can be related to the reduction of a Ag- and Cl- containing film ((Sarkar *et al.*, 1979; Wright *et al.*, 1981), because the sign of the current density is negative, indicating a cathodic selection process. The more noble values for ZCP in the reverse scan can be explained by surface changes during the anodic part of the scan.

The 0.9% saline solution is considered to be more aggresive than saliva and its artificial substrates, because the Cl^- concentration of the latter is 6 times lower (Meyer and Nally, 1975). Moreover, the saline solution does not contain components such as phosphates, which might have a corrosion inhibitive action as well as a buffer capacity (Palaghias, 1985).
Although the degree of segregation and phase composition differed for the five Pd-Ag alloys tested (Mezger *et al.*, 1986), their corrosion behaviour was very similar. Apparently the compositional and constitutional variations are too small to result in substantial electrochemical effects. Although a low current density obtains in the Pd-Ag alloys to potentials of +300 to +400 mV (SCE) and their ZCP is of the same order as high-Pd alloys, the Pd-Ag alloys appear adversely affected by high Cl^- concentrations.
Since the high-Pd alloys are passive/immune to potentials of at least +400 mV (SCE) and do not appear to be affected by Cl^- ion concentration, they may pose less risk in high-duty situations.

5.2.5 Conclusions

The corrosion behaviour of the Pd-Ag alloys investigated was found to be equivalent, Microstructural and compositional differences did not have any significant effect.
In the area of oral interest all alloys showed a sufficient corrosion behaviour. In the more aggressive 0.9% saline solution, excessive anodic overloading might pose problems, since the corrosion behaviour of these alloys was found to be Cl^- dependent, with visible film formation at high Cl^- concentrations.

Acknowledgement

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CHAPTER 6

High-palladium alloys (PART 1)

Metallurgical aspects of high-palladium alloys*

P.R. Mezger
A.L.H. Stols
M.M.A. Vrijhoef
E.H. Greener

Abstract

Nine commercial high-Pd alloys were investigated. Microstructure and phase composition were screened using X-ray diffraction, light microscopy and a scanning electron microprobe. After being etched, some high-Pd alloys revealed dendritic structures. The others showed a more homogeneous structure with distinct grain boundaries. Etching was necessary to reveal distinct structures, though the overall etching effect turned out to be limited. On unetched specimens only a slight chemical heterogeneity could be determined. Except for one alloy, the systems turned out to have complex multi-phase structures. The main face-centered-cubic (fcc) phase was Pd-based. As secondary phases body-centered-cubic (bcc) and/or simple cubic ones were detected. The latter phases were similar to a Cu_3Ga and PdGa intermetallic compound, respectively. Face-centered-tetragonal (fct) structures, as indicated by other investigators, were not found.

6.1.1 Introduction

An alternative treatment modality in porcelain-fused-to-metal prosthetics is the recent development of high-Pd alloys. According to the patent literature the alloy CM Metal (78 wt% Pd, 9 wt% In, 7.6 wt% Sn, 5 wt% Co and 0.2 wt% Si), first sold in the early 1980s, was the precursor of this group of alloys (Boyajian, 1981; Vrijhoef and Greener, 1988). Since then, several high-Pd systems have been introduced (Mezger *et al.*, 1986; Vrijhoef and Greener, 1988), inducing an increasing clinical use and scientific interest (Cascone, 1984; Byrne *et al.*, 1986; Caputo and Matyas, 1986; Odén and Herø, 1986).
Limited information on the microstructural aspects of this group of alloys is available

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(Khabiliyev *et al.*, 1979; Odén and Herø, 1986; Asgar *et al.*, 1986; Vaidyanathan and Prasad, 1987). However, the expanding variety of these alloys demands more comprehensive information. The aim of the present study was to investigate the metallurgical aspects of several commercial high-Pd alloys not studied before.

6.1.2 Materials and methods

Disc-like specimens (15 mm diameter x 2 mm) of the 9 alloys (table 6.1-1) were made according to the instructions of the manufacturer. The specimen size was chosen to represent an upper limit to the clinical thickness requirement of the occlusal aspect and consequently would represent a limiting situation for cooling rates. In order to simulate general practice conditions, all specimens were cast commercially. All alloys received a simulated porcelain-firing heat treatment (F). It consisted of an oxidation treatment, one opaque and two dentin firings under vacuum as well as a glazing procedure at ambient air pressure. Time and temperature for each of these procedures are specified in table 6.1-2. Moreover, some of these alloys were also tested in the as cast condition (AC), because they are also used as a type IV alloy substitute. In this case the alloy generally is used in the as cast condition.

Table 6.1-1 The high-Pd alloys used in this investigation.

Alloy	Code	Manufacturer
Adorpall II	(AD)	Drijfhout, the Netherlands
Albabond E	(AL)	Hereaus, FRG
Argipal	(AR)	Argen, South Africa
A 36	(A3)	Austenal Dental, USA
Bond-on 4	(B4)	Degussa, FRG
Orion Libra	(OL)	Elephant, the Netherlands
Orion Star	(OS)	Elephant, the Netherlands
Orion Vesta	(OV)	Elephant, the Netherlands
Simidur S2	(S2)	Dr. Wieland, FRG

Specimens of the alloys involved were routinely screened under a light microscope (Carl Zeiss, Oberkochen, FRG). X-ray diffraction patterns were obtained using an X-ray diffractometer with a stabilized generator (Philips, Eindhoven, The Netherlands), Cu K_{α}-radiation and a Ni-filter. A Camebax electron microprobe type MB1 (Cameca, Paris, France), coupled to a TN2000 X-ray analysis system (Tracor Northern, Middleton, Wi, USA) was used for microstructural and quantitative energy-dispersive X-ray microanalysis (accelerating voltage 20 kV; stabilized beam current 3.8 nA, take off angle 40°, acquisition 1 minute live time). The elec-

Table 6.1-2 Simulated porcelain firing procedure for the high-paladium alloys.

Alloy	Oxidation phase		Opaque bake*		Dentine bake (twice)*		Glazing	
AD	950°C	5 min	600-940°C	3+4+1 min	600-930°C	6+6+1 min	600-930°C	3+3+1½ min
AL	960°C	5 min	600-960°C	0+6½+½ min	600-940°C	0+6+1 min	600-900°C	0+6+1 min
AR	950°C	10 min*	600-980°C	2+7+1½ min	600-960°C	2+7+¾ min	600-960°C	2+7+½ min
A3	650 980°C	0+8+3 min	760-950°C	0+3½+0 min	760-950°C	0+3½+0 min	760-970°C	0+3½+0 min
B4	960°C	5 min	960°C	3 min	600 960°C	3+4+3 min	700-930°C	0+4+2 min
OL	980°C	10 min	600-980°C	0+7+3 min	600 980°C	0+7+3 min	700-900°C	0+2+2 min
OS	980°C	10 min	600-980°C	0+7+3 min	600-980°C	0+7+3 min	700-900°C	0+2+2 min
OV	980°C	10 min	600-980°C	0+7+ 3 min	600-980°C	0+7+3 min	700-900°C	0+2+2 min
S2	990°C	10 min	860°C	6 min	700 880°C	0+4+2 min	700 900°C	0+2+2 min

* = under vacuum

. + + specimen held for .. min. at lower temperature + temp. is increased to higher value in .. min , + specimen is held at higher temp. for .. min.

tron microprobe was also equiped with one fully focussing universal crystal spectrometer (Cameca, Paris, France) to provide X-ray linescans (accelerating voltage 20 kV; beam current 50 and 200 nA; length of linescan 250 μm; 100 points).
Specimens were examined in a highly polished condition and after etching in aqua regia for 20 sec., since etching was necessary to provide resolution of distinct structures. The results were based on at least 5 measurements per structure. A linear least-squares fit program was used to obtain net elemental peak intensities and a ZAF correction for bulk specimens was executed. Pure elements were used as standards with the exception of Ga, for which GaP was used as a standard. Linescans of selected alloys were made on specimens before and after etching and were also ZAF corrected and referred to the same standards as the bulk studies.

6.1.3 Results

The overall chemical compositions of the distinct alloys as determined by electron probe X-ray microanalysis are depicted in table 6.1-3. No compositional changes were determined due to porcelain-firing. In general the Pd concentration varied between relatively narrow limits (75-79 wt%) along with Au (0-3 wt%). On the other hand, Cu (0-12 wt%), In (0-10 wt%), Sn (0-16 wt%) and Ga (3-10 wt%) varied between wider limits.
The results of the X-ray diffraction measurements are given in table 6.1-4. The main structure found was the Pd-based fcc phase with a lattice parameter in the range of 0.385 to 0.394 nm. The lattice parameter of Pd is 0.389 nm. In two cases (AR and OS) the lattice parameter of the alloy was higher than that of Pd, suggesting Pd-Sn solid solution for AR and a Pd-Sn or Pd-In solid solution for OS, because both In and Sn have a greater atomic radius than Pd. This assignment was confirmed by the results of multiple linescans of unetched and etched specimens of these

Table 6 1-3 Chemical composition (wt%) of the high-Pd alloys in the unetched condition as determined by electron probe X-ray microanalysis Standard deviations are given between brackets.

		Pt	Au	Pd	Cu	In	Sn	Ga	Co	Other
AD	F		2 4 (0 1)	75 7 (1 0)	11 9 (0 3)	1 8 (0 5)		7 3 (0 4)		Co, Ag, Fe
AL	F		1 6 (1 0)	77 2 (0 8)	12 0 (0 5)	1 4 (0 3)	7 1 (0 2)			Pt, Ag, Co, Fe, Zn
AR	AC			79 2 (0 4)			16 0 (0 3)	3 1 (0 3)		Ag, In, Co, Zn, Ru
A3	F		2 3 (0 4)	76 2 (1 4)	10 7 (0 4)			9 5 (0 5)		Ag, Co, Fe, In, Zn, Sn
B4	AC	1 2 (0 7)		77 9 (1 2)	5 4 (0 6)		7 0 (0 4)	5 3 (0 6)		Au, Ag, Co, Fe, In, Ru
B4	F	1 5 (0 3)		78 4 (1 1)	5 6 (0 4)		7 3 (0 6)	6 0 (0 4)		Ag, Fe, In, Ru
OL	AC		2 3 (0 4)	75 9 (1 6)	10 6 (0 4)	4 1 (0 7)	1 1 (0 3)	4 9 (0 9)		Pt, Ag, Co, Ru
OL	F		2 4 (0 2)	76 3 (0 8)	10 4 (0 2)	4 1 (0 5)	1 6 (0 3)	4 8 (0 6)		Ag, Co, Fe, Zn
OS	AC			76 3 (1 4)	4 4 (0 5)	9 5 (0 5)	3 2 (0 8)	3 6 (0 4)	2 6 (0 2)	Ag, Zn
OS	F			76 1 (1 0)	4 4 (0 3)	9 5 (0 8	3 2 (0 3)	3 5 (0 5)	2 7 (0 2)	Ag, Zn
OV	AC		3 1 (0 3)	74 9 (0 8)	11 2 (0 2)			9 6 (1 0)		Ag, Co, Fe, In
OV	F		2 3 (0 1)	77 9 (0 6)	10 9 (0 4)			8 5 (0 5)		Ag, Co, Zn, Ru
S2	AC		29 (0 1)	78 0 (0 5)	10 3 (0 2)			8 4 (0 6)		Fe, In
S2	F		3 1 (0 3)	78 2 (0 5)	10 2 (0 3)			8 2 (0 7)		Pt, Sn, Fe

Table 6 1-4 The lattice characteristics of the phases of the high-Pd alloys detected with X-ray diffraction. Standard deviations are given between brackets.

		Lattice characteristics						
Alloy	Condition	Type	Parameter (nm)		Type	Parameter (nm)		Other phase(s)
AD	F	FCC	0 3857	(0 0005)	BCC	0 3032	(0 0010)	+
AL	F	FCC	0 38478	(0 00009)	BCC	0 3032	(0 0004)	+
A3	F	FCC	0 386	(0 005)	BCC	0 3034	(0 0002)	+
					C	0 4965	(0 0018)	
AR	AC	FCC	0 3933	(0 0002)				
B4	AC	FCC	0 3891	(0 0004)				+
B4	F	FCC	0 3892	(0 0004)				+
OL	AC	FCC	0 3868	(0 0001)				+
OL	F	FCC	0 3874	(0 0004)				+
OS	AC	FCC	0 3910	(0 0001)	C	0 5001	(0 0008)	
OS	F	FCC	0 3905	(0 0006)	C	0 5010	(0 0007)	+
OV	AC	FCC	0 3857	(0 0007)	BCC	0 3035	(0 0006)	+
					C	0 4969	(0 0011)	
OV	F	FCC	0 3857	(0 0007)	BCC	0 3043	(0 0007)	+
S2	AC	FCC	0 3858	(0 0017)				+
S2	F	FCC	0 3865	(0 0013)				+

FCC Face-centered cubic
BCC Body centered cubic
C Simple cubic
AC As cast
F As fired
\+ Indication of additional phases

alloys (tables 6.1-5 and 6 1-6). The X-ray results indicated that no specific stoichiometric relationships were found which would indicate intermetallic compound formation. In the other alloys the lattice parameter was equivalent to or lower than that of Pd, suggesting Pd-Cu solid solutions as the primary fcc phase Since the atomic radii of Ga (0 131 nm) and Pd (0 139 nm) are essentially equivalent, little effect of Ga on the lattice parameter would be expected The lattice parameter of the fcc phase of A3 as fired has a relatively high SD, indicating distortion of the lattice

In addition, secondary phases were seen in most of the other alloys, except for AR The major secondary phases were a bcc structure (a = 0 303 to 0 304 nm) for AD, AL, A3 and OV as well as a simple cubic one (a = 0 496 to 0 501 nm) for A3, OS and OV A weak peak at about 29 5,° which is consistent with the forbidden (100) reflection of the bcc lattice reported, was found for AL (F) and OV (F)

Table 6.1-5 Typical chemical composition ranges (wt%) deduced from linescan data in the unetched and etched condition of alloy OS (F).

Element	Unetched	Etched
Pd	69 - 72	72 - 73
In	8.1 - 10	7.5 - 11
Sn	3.2 - 3.6	3.2 - 4.0
Cu	5.0 - 6.6	5.0 - 6.0
Ga	4.8 - 8.1	4.2 - 9.1
Co	3.9 - 5.1	2.3 - 3.4

Table 6.1-6 Typical chemical composition ranges (wt%) deduced from linescan data in the unetched and etched condition of alloy AR (AC).

Element	Unetched	Etched
Pd	79 - 80	78 - 80
Sn	12 - 18	14 - 17
Ga	2.6 - 8.0	3.1 - 6.5

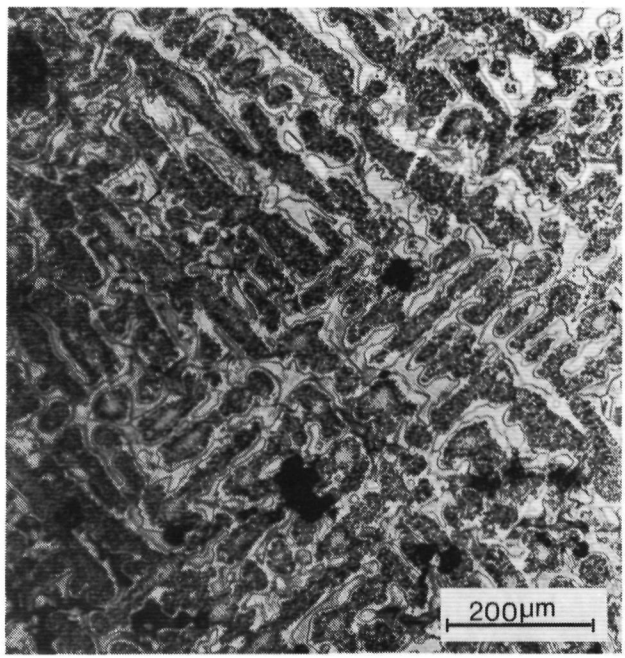

Fig. 6.1-1 Light optical micrograph of A 36 F (100x) in the etched condition. Note the distinct dendritic structure.

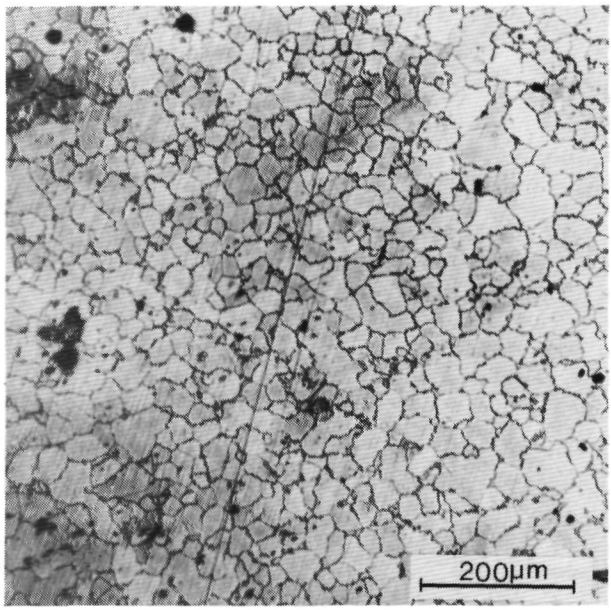

Fig. 6.1-2 Light optical micrograph of Adorpall II F (100x) in the etched condition. Grain boundary etching is evident.

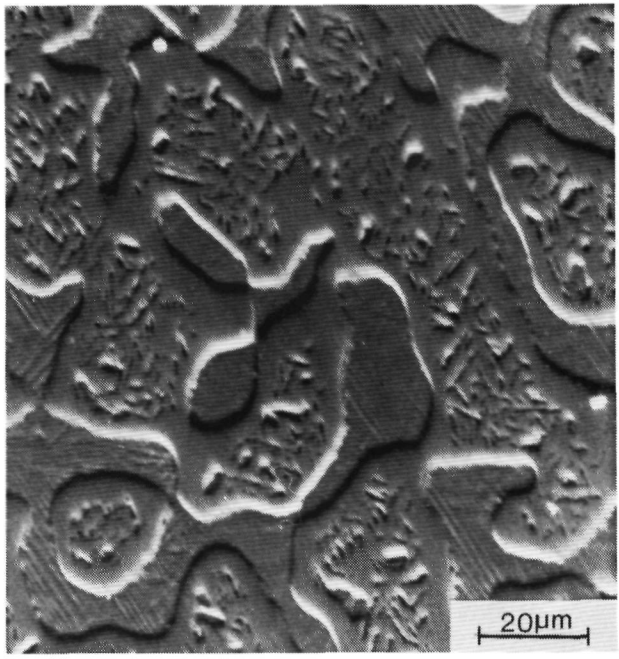

Fig. 6.1-3 Secondary electron image of A 36 F (670 x) in the etched condition. The enlarged dendritic structure from fig. 6.1-1 reveals three structures.

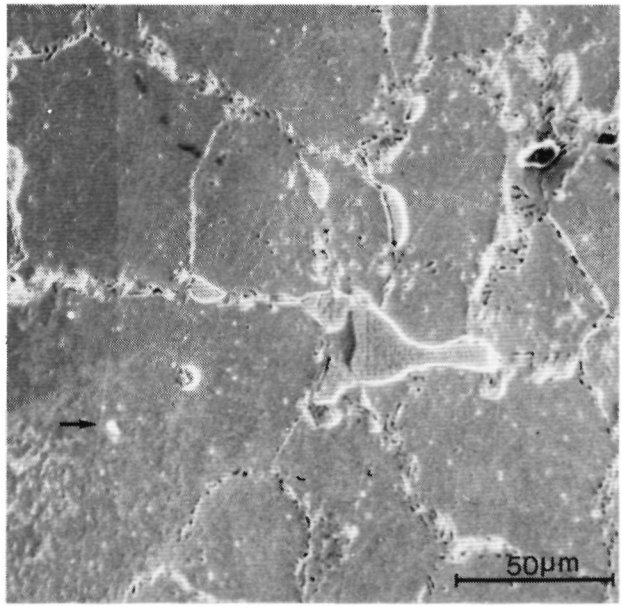

Fig. 6.1-4 Secondary electron image of Adorpall II F (420 x) in the etched condition. Besides the etched grain boundaries and the irregular second structure, the tiny Ru-rich particles can be seen (arrow).

indicating ordering of this lattice structure. Unidentified additional phases, whose concentrations were too low for complete identification, were also seen in all alloys except for AR and OS (as cast).

To reveal the microstructure further, the alloys were etched in aqua regia. Light microscopy showed distinct dendritic structures for alloy A3 (as fired) (fig. 6.1-1), OL (as cast), OV (AC and F) and S2 (AC and F). The other alloys showed a more homogeneous grain structure (fig. 6.1-2) with etching at the grain boundaries. At a larger magnification, using the electron microprobe, the specimens revealed several structures (figs. 6.1-3, 6.1-4). The effect of etching on the chemical composition of the alloys and their structural components, was investigated with the microprobe at different magnification levels (100x and 800x). For the unetched specimens extensive blind probing was necessary, as no alloy structure could be seen. Little influence of etching on the alloy composition could be established, which was confirmed by the linescans. The chemical composition of the different etched structures measured, differed only marginally (tables 6.1-5 and 6.1-6). Therefore, in table 6.1-7 only the matrix phase is shown. In case of AD an incidental Ru-rich structure was detected (fig. 6.1-4). This type of particle contained Ru (57 wt%) and Pd (24 wt%), with minor components such as Cu and Mo.

Table 6.1-7 Chemical composition (wt%) of the matrix phase of the high- Pd alloys as determined by electron microprobe analysis in the etched condition Standard deviations are given between brackets.

		Pt	Au	Pd	Cu	In	Sn	Ga	Co	Other
AD	F		2 8 (0 3)	75 4 (1 1)	11 7 (0 9)	2 3 (0 2)		6 3 (0 6)		Pt, Ag, Co, Fe, Ru, Zn
AL	F		2 3 (0 2)	75 4 (0 8)	13 2 (0 7)	2 0 (0 4)		6 6 (0 9)		Pt, Co, Zn, Ru
AR	AC			80 0 (1 2)			15 8 (0 9)	2 7 (0 6)		Pt, Ag, Cu, In, Zn, Ru
A3	F		2 (1 2)	78 4 (1 3)	9 3 (0 5)			9 4 (0 8)		Pt, Zn, Sn, Ru
B4	AC	1 7 (0 4)		78 8 (0 6)	5 4 (0 6)		7 7 (0 5)	5 3 (0 9)		Au, Ag, Co, Fe, Zn
B4	F	1 4 (0 3)		79 1 (0 8)	5 5 (0 2)	7 3 (0 9)	5 0 (0 7)			Au, Ag, Co, Fe, Ru, Zn
OL	AC		2 5 (0 3)	76 7 (1 2)	10 6 (0 4)	3 9 (0 6)	1 3 (0 8)	4 6 (1 2)		Pt, Co, Fe, Zn
OL	F		2 4 (0 1)	76 8 (0 7)	10 7 (0 4)	3 8 (0 8)	1 6 (0 4)	4 5 (0 2)		Co, Fe, Zn
OS	AC			77 2 (0 5)	3 7 (0 4)	10 6 (0 5)	3 4 (0 8)	2 3 (0 8)	2 6 (0 2)	Pt, Fe
OS	F			76 1 (1 0)	4 1 (0 4)	9 9 (0 9)	2 9 (0 4)	3 1 (1 4)	3 0 (0 2)	Pt, Ag, Fe, Zn
OV	AC		3 0 (0 3)	76 3 (0 5)	12 8 (0 2)			7 5 (0 6)		Pt, Ag
OV	F		2 2 (0 3)	78 1 (0 8)	11 4 (0 3)			7 3 (0 7)		Ag, Co, Fe, Ru, Zn
S2	AC		4 1 (0 6)	76 6 (1 3)	10 3 (1 7)			8 4 (1 6)		Pt, Ag, In
S2	F		2 9 (0 4)	78 2 (1 1)	10 5 (0 8)			7 4 (0 8)		Ag, Co, Fe, In, Zn

6.1.4 Discussion

The differences in the overall chemical composition of the alloys investigated, were found mainly in the Cu, In, Sn and Ga content. One alloy (OS) contained 3 wt% of Co.
From the results of the X-ray diffraction measurements, the complex multiphase character of the alloys, except for AR, is evident. Apart from a fcc matrix phase, a secondary bcc structure was detected for AD, AL, A3 and OV (table 6.1-4). This bcc phase is in agreement with findings of Khabliyev *et al.* (1979) for a Pd-Cu-Ga ternary alloy. The lattice parameter found in this study is similar to the one for the high temperature β-Cu_3Ga phase (Pearson, 1964). Odén and Herø (1986) reported for a commercial Pd-Cu-Ga alloy (very similar to S2 and OV) a Cu-and Ga-enriched (interdendritic) area as did Asgar *et al.* (1986) for three other Pd-Cu base alloys. Their findings are also consistent with the presence of a β-Cu_3Ga structure.
The simple cubic structure indicated in table 6.1-4 for AR, A3, OS and OV (AC), has a lattice parameter close to that of a primary GaPd ($P2_13$) structure (0.488 nm, Pearson, 1964).
For a Pd-Cu-Ga alloy, Khabliyev *et al.* (1979) showed peak configurations which could be consistent with our X-ray diffraction data. However, their indications of tetragonal distortions in the metastable fcc lattice were not found in our results. Moreover, a recalculation of their a and c lattice parameter values on the basis of their peaks does not produce the results they presented. Unfortunately, the face-centered-tetragonal structure indicated by Odén and Herø (1986) is represented without any lattice parameters, so verification was not possible.
The chemical composition of the different structures measured for the high-Pd alloys differed only marginally. On the basis of the X-ray diffraction measurements, areas with distinct chemical compositions corresponding to the primary and secondary phases may be expected. However, they were not found by means of electron microprobe analysis or X-ray linescans, in part because the probe beam diameter exceeded the structure size. The fact that no stoichiometric relationships were observed this way, points at the presence of solid solutions of the matrix fcc phases, as found in the results determining the compositional relationships. Further definition of these Pd compounds remains speculative. The incidental structure found in alloy AD (fig. 6.1-4) where Ru is the major component, is particularly interesting, because Ru cannot be found in the overall chemical composition of the alloy. Ru reportedly functions as a grain refiner in the high-Pd system (Prasad, 1985; Vaidyanathan and Prasad, 1987). The power of Ru as a grain refiner appears to be dependent upon the nominal chemical composition of the alloy (Prasad, 1983, 1985; Vaidyanathan and Prasad, 1987).

Acknowledgement

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CHAPTER 6

High-palladium alloys (PART 2)

The corrosion behaviour of high-palladium porcelain-bonding alloys*

P.R. Mezger
M.M.A. Vrijhoef
E.H. Greener

Abstract

The corrosion behaviour of eight commercial high-Pd alloys was investigated and compared to that of Pd-Ag systems. They were tested with standard potentiodynamic techniques in 0.9% saline solution and an artificial saliva.
The corrosion behaviour of the high-Pd alloys was satisfactory and essentially equivalent. In more severe anodic overloading in 0.9% saline solution this alloy group seemed to be superior compared to the Pd-Ag alloy group Within the high-Pd alloy systems compositional and constitutional variations apparently were too small to result in substantial electrochemical effects.

6.2.1 Introduction

The high-Pd alloys were introduced into the dental market in the early 1980s (Mezger *et al.*, 1986; Vrijhoef and Greener, 1988). Microstructural aspects and a literature review of this group of alloys have been presented elsewhere (Mezger *et al.*, 1988). Aspects of corrosion behaviour of high-Pd alloys get attention in some recent publications (Sumithra *et al.*, 1983; Paradiso, 1984; Lane *et al.*, 1985; Mezger *et al.*, 1985). In these studies a restricted number of corrosion aspects, as well as a small number of high-Pd alloys, are dealt with. However, a comprehensive study of the available alloys in different media is lacking.
It was the aim of this investigation to assess the corrosion behaviour of 8 commercial high-Pd alloys and, when possible, to relate it to metallurgical aspects of the same alloys.

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6.2.2 Materials and methods

The alloys used in this investigation are listed in table 6.2-1. Their respective chemical composition as determined by electron probe X-ray microanalysis, are presented in table 6 2-2. The alloy samples were tested in the simulated porcelain-fired condition according to the manufacturers' instructions.
The phase composition of the alloys investigated is given in table 6 2-3 The main structure found, is the fcc phase with a lattice parameter close to that of Pd In addition, secondary phases were detected. Depending on the system, a bcc and/or a simple cubic phase were found. The latter phases are consistent with a Cu_3Ga and PdGa intermetallic compound respectively. More extensive information on metallurgical aspects is given elsewhere (Mezger *et al.*, 1988).

Table 6 2-1 The high-Pd alloys used in this investigation.

Alloy	Code	Manufacturer
Adorpall II	AD	Dryfhout, Amsterdam, the Netherlands
Albabond E	AL	Hereaus, Hanau, FRG
A 36	A3	Austenal Dental, Koln, FRG
Bond-on 4	B4	Degussa, Frankfurt, FRG
Orion Libra	OL	Elephant, Hoorn, the Netherlands
Orion Star	OS	Elephant, Hoorn, the Netherlands
Orion Vesta	OV	Elephant, Hoorn, the Netherlands
Simidur S2	S2	Dr Wieland, Pforzheim, FRG

Table 6 2-2 Chemical composition (wt%) of the high Pd alloys as determinded by electronic probe X-ray microanalysis

	Pt	Au	Pd	Cu	In	Sn	Ga	Co	Balance
AD		2 4	75 7	11 9	1 8		7 3		Ag, Co, Fe
AL		1 6	77 2	12 0	1 4		7 1		Pt, Ag, Co, Fe, Zn
A3		2 3	76 2	10 7			9 5		Ag, Co, Fe, In, Zn, Sn
B4	1 5		78 4	5 6		7 3	6 0		Ag, Fe, In, Ru
OL		2 4	76 3	10 4	4 1	1 6	4 8		Ag, Co, Fe, Zn
OS			76 1	4 4	9 5	3 2	3 5	2 7	Ag, Zn
OV		2 3	77 9	10 9			8 5		Ag, Co, Zn, Ru
S2		3 1	78 2	10 2			8 2		Pt, Sn, Fe

Table 6 2-3 The lattice characteristics of the phases of the high-Pd alloys as detected with X-ray diffraction Standard deviations are given between brackets

		Lattice characteristics				
Alloy	Type	Parameter (nm)		Type	Parameter (nm)	Other phase(s)
AD	FCC	0 3857	(0 0005)	BCC	0 3032 (0 0010)	+
AL	FCC	0 38478	(0 00009)	BCC	0 3032 (0 0004)	+
A3	FCC	0 386	(0 005)	BCC	0 3034 (0 0002)	+
				C	0 4965 (0 0018)	
B4	FCC	0 3892	(0 0004)			+
OL	FCC	0 3874	(0 0004)			+
OS	FCC	0 3905	(0 0006)	C	0 5010 (0 0007)	+
OV	FCC	0 3857	(0 0007)	BCC	0 3043 (0 0007)	+
S2	FCC	0 3865	(0 0013)			+

FCC Face centered cubic
BCC Body centered cubic
C Simple cubic
\+ Indication of additional phase(s)

Sample preparation, experimental design and details about the electrochemical testing procedures are described extensively by Vrijhoef *et al* (1987) Utilizing these methods, standard deviations of the open circuit potential (OCP) and zero current potential (ZCP) were found to be 50 and 70 mV respectively Coefficients of variation of the corrosion current density (I_{corr}), as well as the current density at a particular overvoltage, are approximately 50%
All alloys were tested in both 0 9% saline solution and in an artificial saliva according to Meyer and Nally (1975)

6 2 3 Results

The corrosion behaviour of all eight high-palladium alloys in cyclic polarization was very similar Typical cyclic polarization diagrams for each electrolyte are given in figs 6 2-1 and 6 2-2 Table 6 2 4 comprises the OCP and the ZCP of the forward scan as well as the I_{corr} in both 0 9% saline solution and the artificial saliva Because the high-Pd alloys are competitive with the Pd-Ag systems, the range of values for the latter ones as represented in another publication (Mezger *et al*, 1986) are depicted as well Within the experimental accuracy, the OCP, ZCP and I_{corr} were equivalent, with the exception of the slightly higher I_{corr} in artificial saliva ZCP was consistently lower than OCP in both solutions Below the ZCP, forward scans displayed a peak at -500 to -400 mV (SCE) in artificial saliva which is absent in 0 9% saline solution The forward scan featured a low current density region ($< 20\ \mu A/cm^2$) from the ZCP to potentials between +400 and +500 mV (SCE)

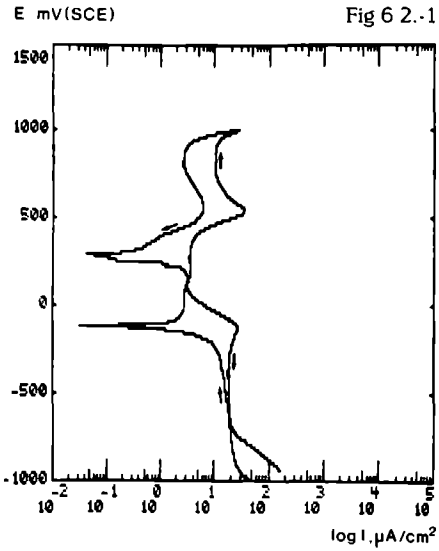

Fig 6 2.-1

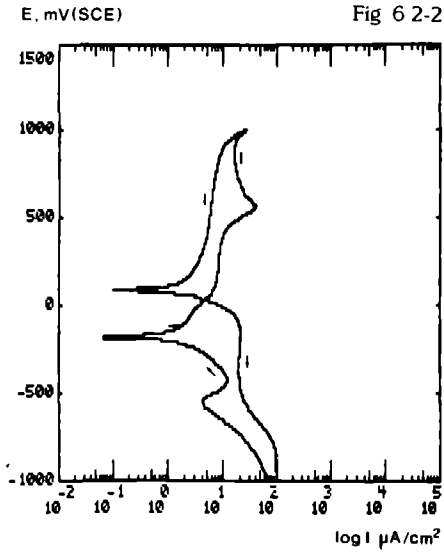

Fig 6 2-2

Fig. 6.2-1 Cyclic polarization diagram of Adorpall II in 0.9% saline solution.

Fig. 6.2-2 Cyclic polarization diagram of Adorpall II in the artificial saliva.

Increasing the anodic overpotential produced a peak in current density at ca. 600 mV (SCE) and current densities varying from 40 to 230 $\mu A/cm^2$ in 0.9% saline solution and 20-40 $\mu A/cm^2$ in artificial saliva (table 6.2-5). Upon scan reversal at +1000 mV (SCE) a peak was again seen at ca. +600 mV (SCE) in 0.9% saline solution, but not in artificial saliva. A slight indication of current density increase

Table 6.2-4 OCP (mV vs SCE), ZCP (mV vs SCE) and I_{corr} ($\mu A/cm^2$) of the high-Pd alloys in 0.9% saline solution and in artificial saliva.

	OCP	ZCP	I_{corr}	OCP	ZCP	I_{corr}
Alloy	0 9% saline solution			Artificial saliva		
AD	−30	−120	0.05	+ 60	−180	0.07
AL	− 20	−120	0 03	+120	−230	0.10
A3	+130	−180	0 05	+ 50	−80	0.09
B4	+130	−140	0.06	+150	−190	0.06
OL	+40	−180	0.15	+ 10	−140	0.12
OS	+ 80	−200	0.17	+120	−180	0.37
OV	+ 40	−140	0.08	+ 90	−220	0.07
S2	+110	−230	0.04	+120	−230	0.05
Pd-Ag	−20/	−280/	0.03/	−30/	−200/	0.04/
(range)	+ 90	−140	0.10	+ 60	−130	0.14

Table 6.2-5 Anodic peak potentials (PP), their corresponding current density (PC) along with current density values at +400 mV (SCE) of the high-Pd alloys for 0.9% saline solution and an artificial saliva.

	$I_{400\,mV}$	PP	PC	$I_{400\,mV}$	PP	PC
Alloy	0 9% saline solution			Artificial saliva		
AD	47	+550	35	9 8	+560	40
AL	2 1	+590	17	18 6	+520	24
A3	4 4	+650	27	4 1	+660	40
B4	6 3	+560	22	12 8	+520	35
OL	18 4	+640	110	6 2	+660	36
OS	6 1	+550	28	7 6	+550	28
OV	5 9	+570	130	12 8	--	--
S2	9 2	+650	230	8 3	+570	45
Pd-Ag	8 4/	+530/	850/	8.6/	+440/	21/
(range)	324	+600	2300	19	+510	43

was seen in case of AD, AL, OL, OV and S2 at −50 to −100 mV (SCE) in 0.9% saline solution, but not in artificial saliva. The anodic peak in the reverse scan showed a current density significantly lower than that observed in the forward scan. No anodic peaks occurred for OV in artificial saliva In this case the current density stayed at a constant level which was reached early in the anodic scan.

6.2.4 Discussion

In general the zero current potential (ZCP) was in the order of 100 to 330 mV lower than the open circuit potential This discrepancy may be related to the spontaneous passivation of the alloys, either in terms of a film formed after polishing or upon direct immersion. Cathodic polarization at -1000 mV (SCE) may be expected to reduce some of this film and, thus subsequently, depress the measured corrosion potential.

Based on the accuracy of the OCP measurement, the difference between the most noble alloys (B4, A3) and the most active (AD and AL) are at the $p< 0\ 05$ boundary.

The discrepancy between the 10 minute OCP presented earlier (Mezger *et al.*, 1985) for B4 and OL in the same electrolytes and the less noble values found in this investigation is noteworthy. Small differences in composition can produce large effects in OCP. The nature of the polarization profiles, however, are similar, confirming that polarization techniques are more appropriate means of studying electrochemical phenomena than reliance on OCP alone.

I_{corr}, which gives an indication for the corrosion resistance of a system allowed to function in an isolated position, was in the same order of magnitude in both electrolytes used and values were in the range determined for Pd-Ag PFM alloys (table 6.2-4). For OS (the only Co-containing alloy) I_{corr} appears to be higher than the values of the other alloys in artificial saliva.

All alloys were immune or passive in the stagnant aerated Cl^- and artificial saliva solutions to at least potentials of +400 mV (SCE). In this region current density values stayed low, seldom exceeding 10 $\mu A/cm^2$. A possible area of oral interest was indicated in literature (Ewers and Greener, 1985; Corso *et al.*, 1985) with an anodic border value of +300 mV (SCE). For all alloys investigated no problems are likely to arise under normal clinical conditions. Even under more severe anodic overloading a sufficient fail-safe-zone seems present. Beyond +400 mV (SCE) a current density increase occurred for all alloys in both solutions. The resulting peak values around +600 mV (SCE) are in the same order of magnitude. Only for OL, OV and S2, the peak current density exceeded 100 μ A/cm^2 in 0.9% saline solution. In artificial saliva the peak current density for all alloys was in the range of 24-45 $\mu A/cm^2$. This observation is in sharp contrast to that seen in Pd-Ag PFM alloys, where a peak current density difference of 10 to 100 times was seen between 0.9% saline solution and artificial saliva. The Cl^- effect in those alloys was attributed to formation of a Ag Cl film.

The current density peak occurring at +600 mV (SCE) is in agreement with work on pure Pd (Shan Shih, 1983) and some high-Pd alloys (Sumithra *et al.*, 1983) in 1% saline solution. However, Sastri *et al.* (1982) did not resolve a similar peak in current density when measuring Pd in the same electrolyte. The current density increase at about +400 mV (SCE) in our study, might be related to the $Pd/PdCl^{2-}$ equilibrium potential given by the reaction $Pd + 4Cl^- \rightarrow PdCl_4^{2-} + 2e$. $E^\circ = +380$ mV (SCE) as indicated by Sastri *et al.* (1982) in relation to pure Pd in a 10% saline solution.

This mechanism may occur since Pd cations were detected by atomic absorption in solutions created by anodic polarization at +500 mV (SCE) for 24 hours of two of the alloys B4 and OL (Vrijhoef and Greener, 1988).

Another mechanism might be the attack on a Cu-containing bcc phase and/or a Ga-containing simple cubic phase.

The fact that current density during the reverse scan was lower than that of the anodic part of the forward scan, indicates electrochemical behaviour, which may be associated with resistance against pitting or the build-up of an effective protective layer (Galvele, 1983). In some alloys a slight indication of an anodic reverse peak occurred in the same potential range as during the forward scan. It indicates some further corrosion attack. The more noble values for ZCP during the reverse scan can be explained by surface changes during the anodic part of the scan, resulting in a surface enrichment of the cathodic phase. Metallographic etching of these Pd alloys revealed a structure in which only the primary Pd solid solution phase could be found, confirming the existence of more active areas formed by the lower melting point phases. An analogous situation might exist following corrosion induced by the polarization scan.

The slight indication of current density increase in the cathodic part of the reverse scan could have pointed at reduction of copper as described by Wright *et al.* (1981) for a Au-Cu alloy with 90 at. % Cu. However, unpublished data on a high-Pd alloy without Cu did also show the same phenomenon.
The 0.9% saline solution is considered to be more aggressive than saliva and its artificial substitutes, because the (Cl^-) which is 6 times higher (Meyer and Nally, 1975). Moreover, it lacks components which might show a corrosion inhibitive action and a buffer capacity such as phosphates (Palaghias, 1985). It might be expected that the high-Pd alloys will be more resistant to excessive electrochemical overloading than the Pd-Ag systems.
In general it might be stated that the different microstructure and phase composition of the respective high-Pd alloys did not reflect in their corrosion behaviour. Apparently, the compositional and constitutional variations are too small to result in substantial electrochemical effects. Evidently the difference in trace elements added to control grain size, castability etc. do not substantially affect electrochemical behaviour.

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CHAPTER 7

Laboratory prognosis versus preliminary clinical performance

This chapter consists of three parts. The first part comprises the introduction of two additional alloys, not included in the second chapter.In the second part, these and the experimental alloys from chapter 4-6 are fitted into the alloy spectrum described in chapter 2. The third part consists of the preliminary results of a clinical trial. In this clinical part, the influence of the oral environment on cast restorations was evaluated. After removal of the restorations from the mouth, further laboratory screening gives an insight into the relation between the in vivo corrosion behaviour and the in vitro corrosion testing from the preceeding chapters.

7.1 Two outliers from the casting alloy gamut

Two materials, aluminium-bronze and titanium, were additionally selected for the clinical trial. While both of these alloys see limited clinical use currently, they are not accepted as part of the current spectrum of casting alloys for different reasons. These interesting outliers are therefore introduced separately in this chapter and their corrosion behaviour under laboratory conditions is included.

7.1.1 Aluminium-bronze casting alloys

Two types of casting alloys with an extremely high copper content are described in dental literature: copper-zinc and aluminium-bronze alloys. After some initial favourable reports (Fusayama *et al.*, 1965; Ismaïl and Lyon, 1973), research on corrosion and microstructure of copper-zinc alloys (Sarkar *et al.*, 1978; Sarkar, 1981) and adverse in vitro and clinical findings on gold plated screwposts of similar alloys (Gjerdet and Espevik, 1977; Arvidson and Wröblewski, 1978) elicited doubts on the advisability of eventual widespread clinical use.
The aluminium-bronze alloys were introduced in dentistry in the 1920's. Though this type of alloy is certainly not a generally accepted type of market alloy, it is commercially available and reportedly may be found in extensive use in some countries (Nakayama *et al.*, 1984). A renewed interest in these alloys is also evident in the recent literature (Thomson, 1982; Thomson *et al.*, 1983; Nakayama *et al.*, 1984; Mueller and Barrie, 1985, 1987; Joshi *et al.*, 1987). For these reasons additional research is needed.

7.1.2 Titanium

Pure titanium and its alloys are widely used for industrial purposes Their application in general medicine and dentistry as implant materials is well known (Williams, 1981, Weber, 1985) The biological and corrosion characteristics are generally considered to be favourable (Mueller and Greener, 1970, Williams, 1981, Weber, 1984, Rae, 1986a and b, Hruska, 1987) Up to now, the application of titanium in crown and bridgework is very limited, due to the difficult and expensive techniques involved Titanium has an extremely high melting point (about 1670°C), a low specific weight and extreme oxidation characteristics at high temperatures Therefore, adapted investment materials and casting devices are needed Its physical properties are changed by oxidation, even when casting is done under a relatively pure argon atmosphere (Ida *et al*, 1985) Porcelain-firing on pure titanium is not easy, because of its oxidation characteristics and low expansion coefficient Adapted porcelains with low coefficients of thermal contraction and a low fusion temperature are needed (Menis *et al*, 1986, 1987) Recently, an intra-oral welding device for titanium was introduced by Hruska (1987) Without any technical details the same author indicated the possibility for complex porcelain-fused-to-metal bridgework

7.1.3 Materials and methods

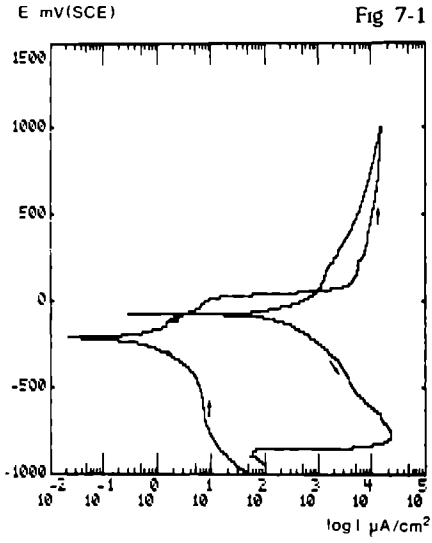
As an example of aluminium-bronze alloys, Trindium (Trindium Co , New York, USA) was chosen Its chemical composition comprises 87 7% (wt%) copper, 10 1% (wt%) aluminium, 1 2% (wt%) nickel and a balance of several elements The in vitro electrochemical corrosion testing procedure used for pure titanium and Trindium is described in chapter 2

7.1.4 Results and discussion

Cyclic polarization diagrams for Trindium and pure titanium typical for both test solutions, are given in figs 7-1 and 7-2 The electrochemical data are shown in the tables 7-1 to 7-3

Table 7-1 Current densities in $\mu A/cm^2$ of Trindium and titanium at several potentials (mV vs SCE) in 0 9% saline solution

	Potential						
Alloy	−100	0	100	200	300	400	500
Trindium	448	7120	1580	2530	1890	1860	2090
titanium	1 3	1 8	1 7	1 6	1 7	1 8	2 0



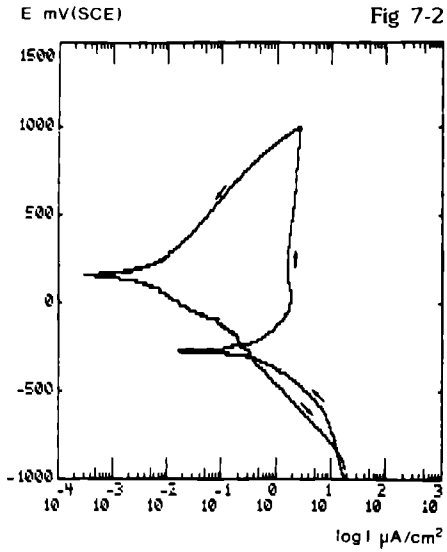


Fig. 7-1 A cyclic polarization diagram of Trindium in 0.9% saline solution.

Fig. 7-2 A cyclic polarization diagram of titanium in 0.9% saline solution.

The OCP and ZCP values for both materials were in the range of the base metal alloy group, as shown in chapter 2. The extrapolated I_{corr} value of Trindium in 0 9% saline solution was among the highest values seen in this study. The corresponding value in artificial saliva was well within the general alloy spectrum range (0.01 to 0.43 μA/cm2) as presented in chapter 2. The I_{corr} for titanium in both solutions was low. Anodic potential excursions from the ZCP for Trindium in both solutions showed an almost immediate increasing current density, indicating active behaviour (fig. 7-1) Titanium on the other hand, remained totally passive over the whole anodic range investigated (fig. 7-2). During the anodic part of the reverse scan, the current density of both alloys was lower than in the forward scan for both electrolytes. So, no tendency to pitting was evident. From the corrosion data shown here, Trindium and titanium may be ranged at almost opposite sites of the corrosion spectrum.

Table 7-2 Current densities in $\mu A/cm^2$ of Trindium and titanium at several potentials (mV vs SCE) in artificial saliva.

	Potential						
Alloy	−100	0	100	200	300	400	500
Trindium	1 9	8 2	4110	5590	7970	8960	10400
titanium	0 2	0 4	0 8	1.4	2 2	2 4	2.4

Table 7-3 OCP (mV vs SCE), ZCP (mV vs SCE) and I_{corr} ($\mu A/cm^{2}$) of Trindium and titanium in 0.9% saline solution and artificial saliva.

	0 9% saline solution			Artificial saliva		
Alloy	OCP	ZCP	I_{corr}	OCP	ZCP	I_{corr}
Trindium	-250	-347	3.3	-128	-211	0 25
titanium	-232	-271	0.09	-94	-191	0.08

7.2 Positioning of the experimental casting alloys in the corrosion spectrum of the current market alloys

The corrosion profiles of the alloys as presented in chapter 2 and the chapters 4 to 6 are compiled in figs. 7-3 to 7-11. Titanium and Trindium, the aluminium-bronze alloy, not included in these representations, will be integrated in the text. In fig. 7-3 to fig. 7-11 the range of values is indicated by the minimum and the maximum for each alloy group. Also the median values are shown.

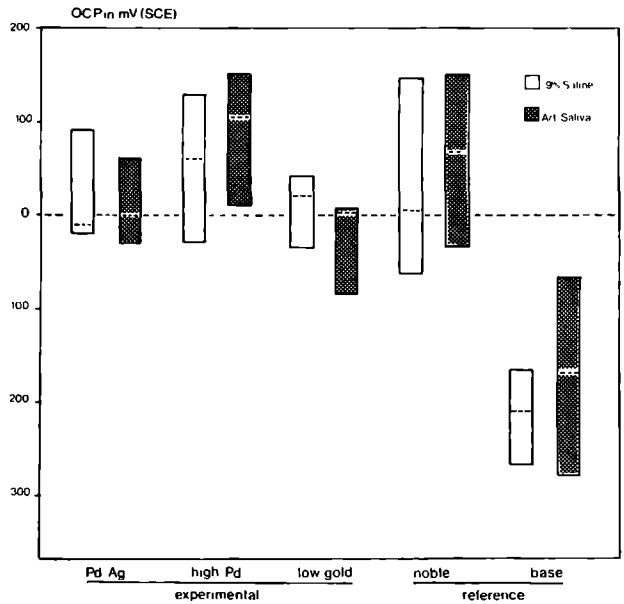


Fig. 7-3 Minimum and maximum values of the open-circuit potential (OCP) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

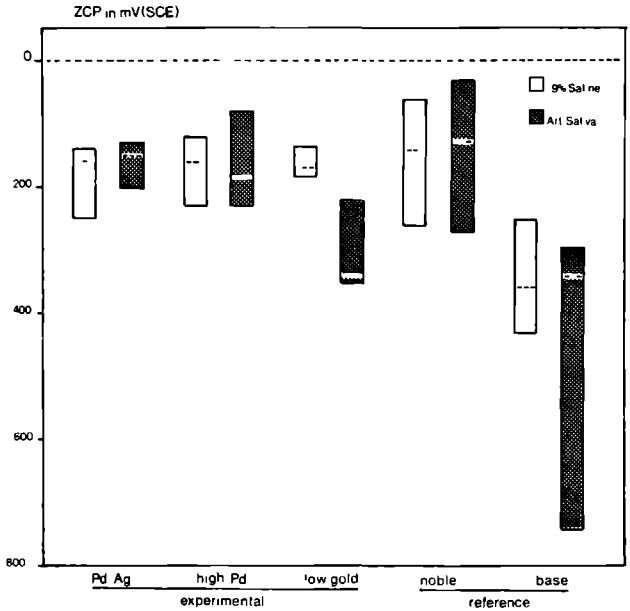


Fig 7-4 Minimum and maximum values of the zero current potential (ZCP) of the different alloy groups in 0 9% saline solution and the artificial saliva The median value is indicated by a dotted line within each bar

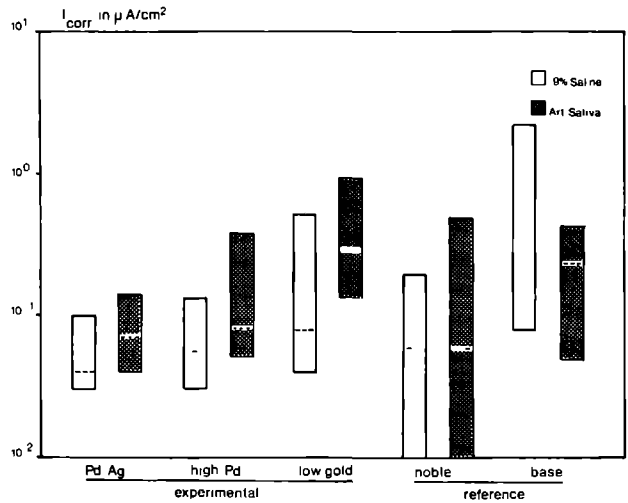


Fig 7-5 Minimum and maximum values of the corrosion current density (I_{corr}) of the different alloy groups in 0 9% saline solution and the artificial saliva The median value is indicated by a dotted line within each bar

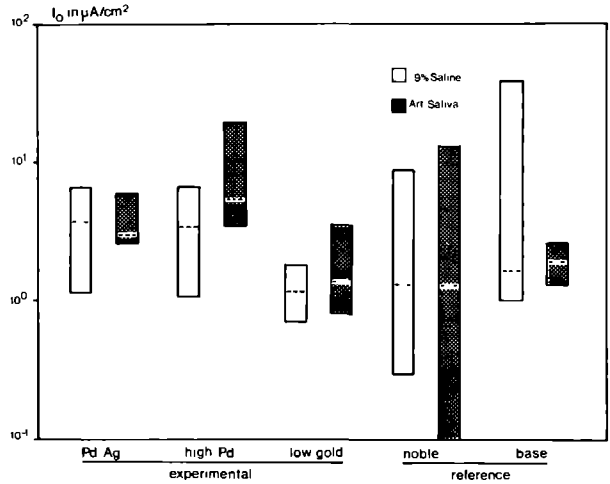


Fig. 7-6 Minimum and maximum values of the current density at 0 mV (SCE) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

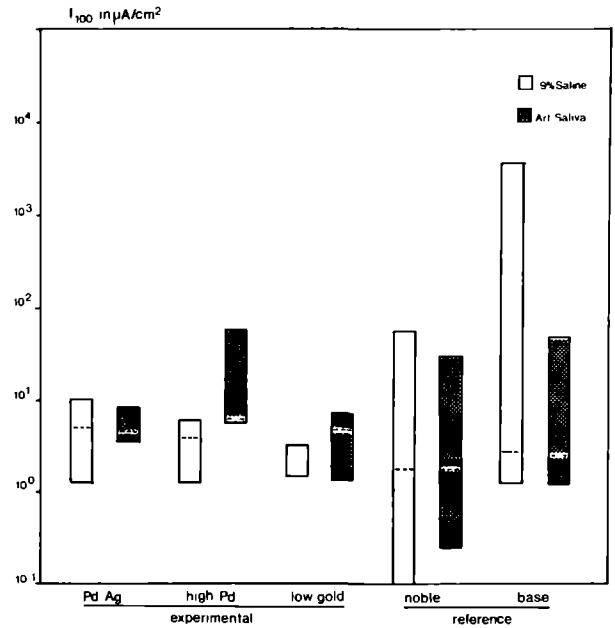


Fig. 7-7 Minimum and maximum values of the current density at +100 mV (SCE) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

It is evident that in the effort to simplify and to delineate the alloy spectrum, groups of alloys become rather heterogeneous in chemical composition. This applies to the noble and to a lesser extent also to the base metal group presented in chapter 2. The heterogeneous character is reflected in the ranges of corrosion values found within these groups.

From fig. 7-3 and fig. 7-4 it is evident that the OCP and ZCP values of the experimental palladium-enriched alloys belong in the range of the noble alloy group. Titanium and Trindium show values (tables 7-2 and 7-3) similar to that of the base metal alloys.

The corrosion current density (I_{corr} in fig. 7-5) shows small variations in value for the Pd-Ag and high-Pd alloys. In the small yellow low-gold group the higher I_{corr} of Mirafort 3L is responsible for the large range evident in both solutions. The aluminium-bronze alloy shows the highest I_{corr} value encountered in 0.9% saline solution. In artificial saliva its value falls within the range of current market alloys. Titanium shows low I_{corr} values in both electrolytes.

From fig. 7-6 to fig. 7-11, derived from the cyclic polarization scans, it is evident that up to an anodic boundary value of +300 mV (SCE), the corrosion behaviour of all the experimental Pd-enriched alloys is within the range of acceptability. Under more extreme conditions of anodic overloading (fig. 7-10 and fig. 7-11), distinct current density increases show for the yellow low-gold alloys in both electrolytes used. The same goes for the Pd-Ag alloy group in 0.9% saline solution.

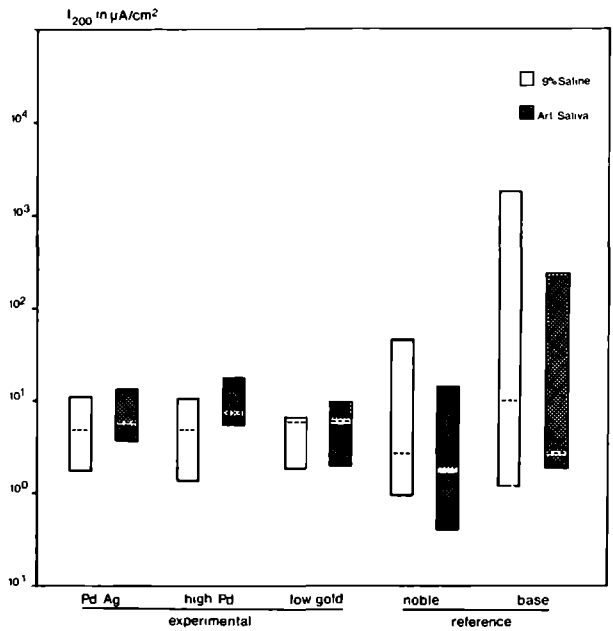


Fig. 7-8 Minimum and maximum values of the current density at +200 mV (SCE) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

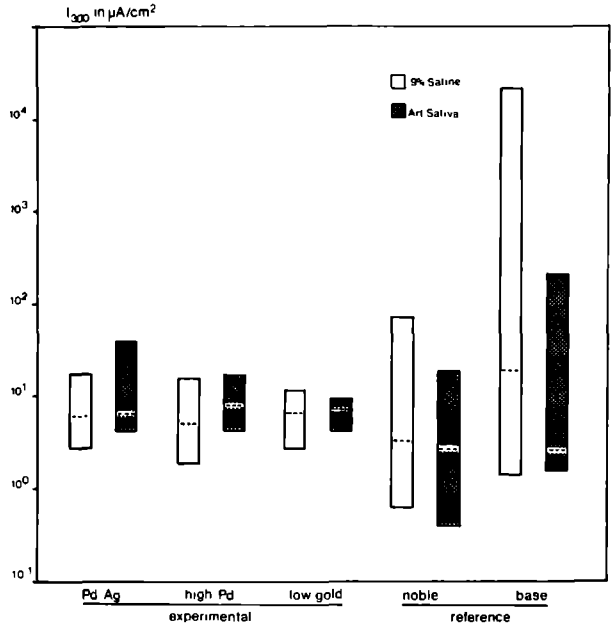


Fig. 7-9 Minimum and maximum values of the current density at +300 mV (SCE) of the different alloy groups in 0.9% saline solution and the artificial saliva The median value is indicated by a dotted line within each bar.

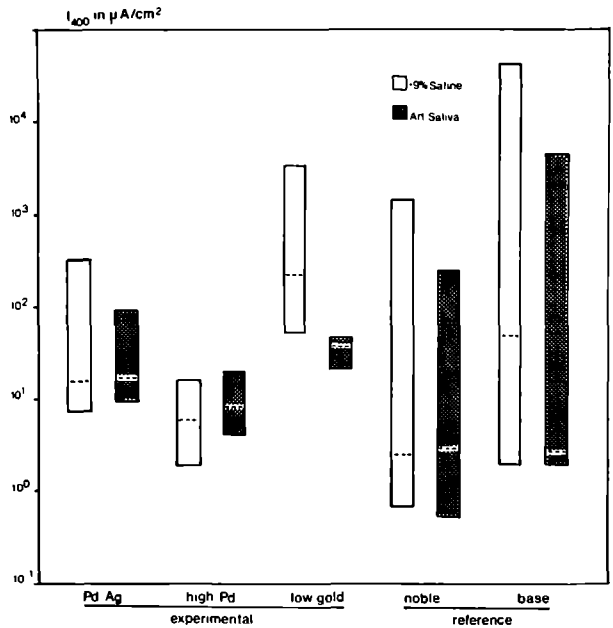


Fig. 7-10 Minimum and maximum values of the current density at +400 mV (SCE) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

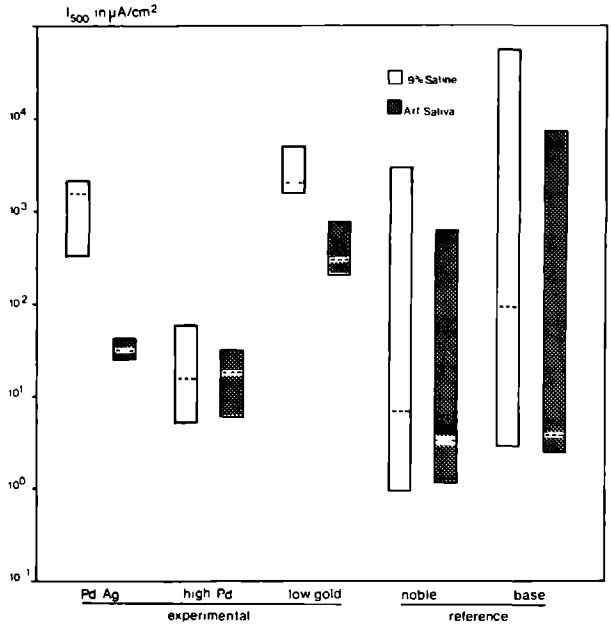


Fig. 7-11 Minimum and maximum values of the current density at +500 mV (SCE) of the different alloy groups in 0.9% saline solution and the artificial saliva. The median value is indicated by a dotted line within each bar.

The heterogeneous character of both the noble and base metal alloy groups from chapter 2 is shown under these extreme conditions by the extent of the respective bars in fig. 7-10 and fig 7-11.
The aluminium-bronze alloy shows an immediately active behaviour in the whole anodic range for both electrolytes, as indicated by large current densities. The completely passive behaviour under conditions of anodic overloading of titanium and its low current densities are exemplary.
Upon scan reverse neither the Pd-enriched alloys nor Trindium and titanium display an irreversible electrochemical behaviour or phenomena associated with pitting or lack of protective film in both electrolytes.

7.3 Selection of alloys for the clinical trial

To be used in a clinical trial, some examples from the alloys included in chapter 2 were selected to figure as 'reference alloys' for the systems, described extensively in chapter 4-6. Auropall IV was chosen as an accepted gold-reduced alloy with a corrosion profile fairly representative for Class 3 to 1 type III/IV casting alloys. Talladium is a beryllium containing nickel-chromium alloy and as such an accepted porcelain-fused-to-metal casting alloy. Moreover, this type of material is widely used in the realm of adhesive bridges (Thomson, 1982; Hill *et al.*, 1986). The in

vitro corrosion resistance of this particular alloy is situated in the lower end of the corrosion spectrum.
Two representatives of the accepted older alternative silver-palladium casting alloy group (Class 0) were included: Palliag M and WLW. Landesman *et al.* (1981) indicated in a clinical experiment, that the latter alloy showed more discoloration and signs of pitting than a conventional type III/IV control alloy. According to laboratory and in vivo investigations, silver-rich areas of the Ag-Pd type of alloy are tarnish prone (Niemi and Holland, 1984; Niemi and Herø, 1985; Herø and Niemi, 1986).
From the experimental palladium-enriched alloy groups, Mirafort 3L was chosen as a yellow low-gold alloy, Ceram W-1 as representative for the palladium-silver group and Adorpall II and Orion Vesta as examples of the high-palladium alloys. Moreover, titanium and the aluminium-bronze alloy (Trindium) were included in the clinical trial. In table 7-4 the alloys used are summarized.

Table 7-4 The alloys included in the short-term clinical trial.

Type III/IV alloys	PFM alloys
Auropall IV	Ceram W1
Mirafort 3L	Adorpall II
Palliag M	Orion Vesta
WLW	Talladium
Titanium	
Trindium	

7.3.1 Design of the experiment

During a clinical trial, cast restorations were made after an informed consent procedure. Ten patients, varying in age from 29 to 37 years with a good general health, participated. Their dental history included (extensive) amalgam treatment while, with one exception, no cast restorations were present at the start of the experiment. All participants had a good dental health, but needed in general several cast restorations for long-term stabilization of the occlusion. A total of 28 full/partial veneer and porcelain-bonded castings was inserted in the premolar and molar region for a period of 14 to 22 months. The alloys selected for this experiment were assigned at random to the trial subjects.In case a type III or IV alloy had to be placed in a high visibility region, resin facings were used. Whenever possible, various casting alloys were used in the mouth of each patient. In this way a clinical situation with different metallic (cast and amalgam) restorations was created, not precluding possible electrogalvanic phenomena.

The cast restorations were made according to the procedures of the department of Occlusal Reconstruction (Käyser *et al*, 1985) and cemented with zinc-phosphate cement (Standard Dental Products, The Hague, The Netherlands) During the experiment no professional prophylaxis was executed on the test teeth.
During the clinical period, a 6 month recall system was used, starting at least 2 weeks after insertion of the restoration. During the control session, first the findings of the patient were registered, followed by explicit questions about oral sensations commonly related to electrogalvanism (e g. smarting, burning, electrical sensation or metallic taste). The direct environment of each cast restoration in terms of approximal and antagonistic contact materials was noted. Photographs of the restorations were taken at each control session. The size and set-up of the alloy- and the corrosion- oriented experiment precluded a meaningful assessment of e g periodontal aspects. An attempt to distinguish the influence of the casting alloy or its corrosion products on the periodontal condition from the influence of plaque and the physical presence of subgingival crown margins seems futile However, to be aware of not expected extreme periodontal changes, some measurements were included in this study A constant force (max 25 gf) periodontal probe (Borodontic, Borident B.V., The Netherlands) was used to test the teeth restored with a cast restoration and a similar control tooth on the contralateral side of the same jaw. Pocket depth, periodontal attachment level, papilla bleeding index

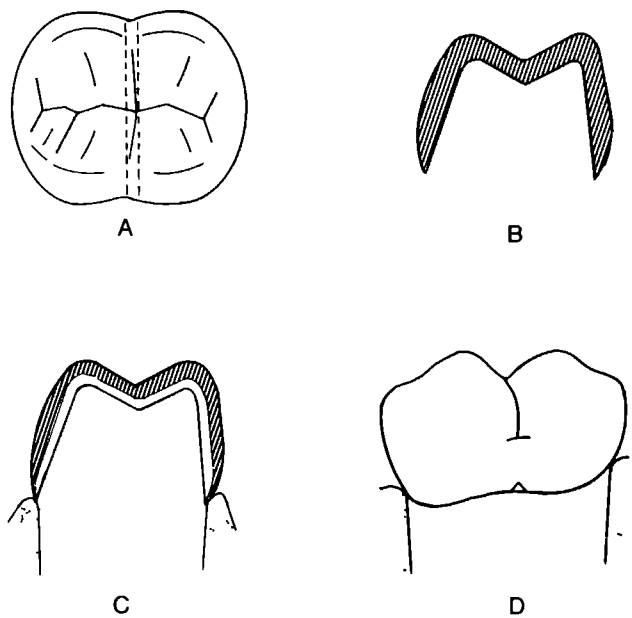


Fig. 7-12 Modification of crown thickness to facilitate removal in the clinical study.
A: occlusal view with indication of internal relief groove
B: bucco-lingual section of normal crown.
C: internal reduction groove as indicated on A
D: external indication of crown reduction site

(PBI according to Mühlemann, 1978) and the presence of subgingival plaque (two point scale) were assessed at 4 sites interproximally. Moreover, on the buccal and lingual surface subgingival plaque and gingival bleeding tendency were scored (two point scale). To relate the presence of plaque to metal discoloration, the plaque index according to Sillness and Loe (1964) was used buccally and lingually. The place of the restoration margin compared to the gingival outline, was measured on the middle of the buccal and lingual tooth surface next to the V-shaped indentation.
Discoloration and roughness of the surface of the cast restorations were assessed with 4 point scales, used previously by Letzel *et al.* (1983) and Mezger *et al.* (1985). After the trial period the crowns were removed to enable laboratory testing. To facilitate their removal, a relief groove was made on the internal surface of the casting, extending from the middle of the buccal to the lingual surface and ending in an externally visible V-shaped indentation on the margin (fig. 7-12). So a quick removal of the restoration, without damaging the outline of the preparation, was performed. In the same session a permanent crown, made on the original technique model, could be cemented. The experimental crowns were photographed again after removal from the mouth of the patient. Photographic representation of the removed crowns turned out to be difficult, because of the reflection of light on the curved crown surfaces. Using an indirect light source, wear facets may be accentuated, but the crown surface becomes slightly dull. The photographs, presented in the results section, are attuned to each other. The external crown surface was scrutinized macroscopically, under the stereo light microscope (Wild, Heerbrugg, FRG) with a maximal enlargement of 50x and with the scanning electron microscope (PSEM 500, Philips, Eindhoven, The Netherlands).

7.3.2 Results of the clinical study

Screening of the experimental restorations on the laboratory model at baseline, revealed some macroscopic porosities in the Mirafort 3L castings. Also for one Orion Vesta and one titanium restoration some porosities were evident. At insertion the titanium crowns did not show the same degree of lustre as the other castings. In general, tiny scratches may be noted on the alloy surface resulting from the laboratory polishing procedure, irrespective of the choice of alloy. Under a stereo microscope, most castings showed pores. This seems to be a general phenomenon.
During the clinical study, the patients were asked to report anything unusual about their (dental) well-being. As a result, one endodontic treatment had to be executed through a cast restoration on a premolar, with a history of very extensive amalgam treatment and partial cusp fracture. Some temporary tooth sensivity was noted. One patient experienced this sensitivity during the treatment stage and a long period afterwards, irrespective of the choice of casting alloy. However, after the trial period permanent restorations could be placed without any additional treatment.

Observations by the trial subjects related to the cast restorations were scarce A metallic taste sensation with chewing gum was observed in one case during the first months after insertion at the side of the jaw, where a yellow low gold (Mirafort 3L) restoration was in contact with both a high-palladium (Adorpall II) crown and amalgam restorations At one control session, one patient reported a warm sensation between a silver-palladium (Palliag M) and an aluminium-bronze (Trindium) crown while chewing gum One Mirafort 3L restoration was 'just too smooth, as if it did not really belong in the mouth However, it was not a real source of complaint The periodontal measurements did not reveal unusual changes

Clinically, discoloration was often found on the cervical part of the lingual metallic surface of a cast restoration, extending onto the proximal surfaces It manifested itself by a loss of lustre and/or a discolored film formation

As all alloys showed some tendency to colour change as measured clinically with the 4 point scale, a statistical evaluation using an one side Pearson correlation test could be used It revealed a significant relation between the plaque index scored at the lingual metal surface and the degree of discoloration ($r = 0\ 40$, $p = 0\ 025$)

After crown removal it became all the more clear, that also deposits of debris and plaque were clinically scored as discoloration Clinical measuring of colour aspects only included the occlusal and lingual or buccal surfaces, not covered with porcelain or resin Proximal surfaces were assessed after crown removal Combining the results of clinical measurements with macroscopic assessment in the laboratory, Auropall IV, Mirafort 3L, Palliag M, Trindium and WLW showed somewhat more colour change than the porcelain-fused-to-metal alloys and titanium The proximal discoloration was primarily found below the contact area and was often combined with a distinctly dulled surface due to deposits (debris, plaque)

The assessment of roughness in the clinical situation was often dominated by the aspect of the occlusal surface, where functional and parafunctional aspects of wear play an important role Again the screening under laboratory conditons provided additional information The degree of roughness of the Mirafort 3L crowns increased during the clinical period Light microscopy after crown removal showed a rough and pitted occlusal aspect (fig 7-13) The other external crown surfaces became dull (figs 7-13 and 7-14) During the trial period the aluminum-bronze (Trindium) crowns showed also increasing roughness (fig 7-15) For this alloy, a patient effect was obvious In 2 out of 3 crowns the non-occlusal surfaces became completely dull and occlusal roughness and pitting was evident under the stereo microscope The third crown remained glossy Irrespective of the change of luster, all the Trindium crowns revealed a distinct microstructure at low magnifica tions (> 12x) over the whole alloy surface (fig 7-16), even on the attrition facets

The other alloys showed varying roughness related to occlusal wear facets (figs 7-17 to 7-19), combined with reasonably glossy surfaces displaying local tiny scratches resembling those made during polishing in the dental laboratory

Talladium showed a smooth clinical appearance, but light microscopy (magnification >12) displayed large areas with a distinct microstructure (fig 7-20) At a larger magnification level (420x) in the scanning electron microscope, the typical matrix and NiBe phase could be observed (fig 7-21)

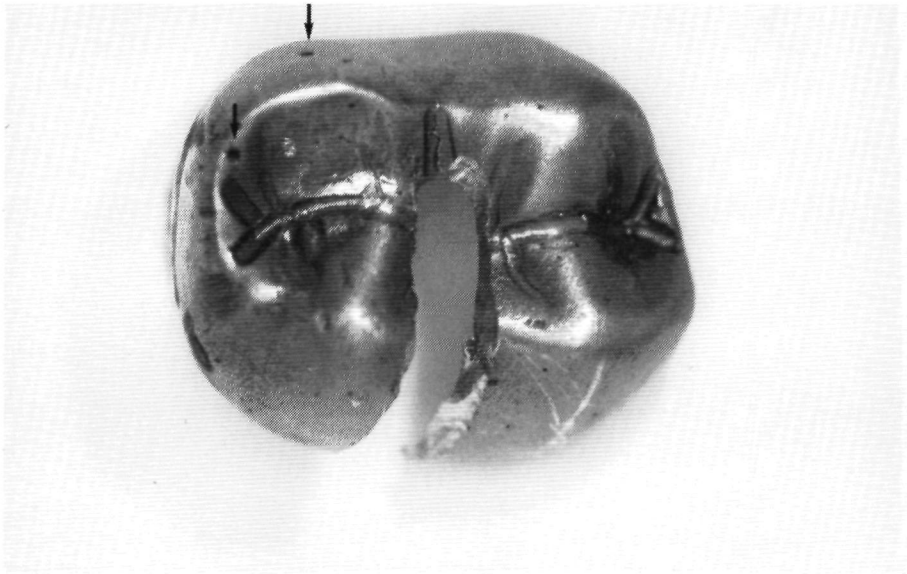


Fig. 7-13 A yellow-low gold (Mirafort 3L) crown, after 14 months of clinical use. Note the casting porosities (arrows) and the dull buccal crown surface.

Fig. 7-14 A Mirafort 3L crown after 14 months. The dull lingual aspect and some porosities are evident.

Fig. 7-15 Roughness and pitted wear facets and a dull aspect of an aluminium-bronze (Trindium) crown after a clinical period of 22 months.

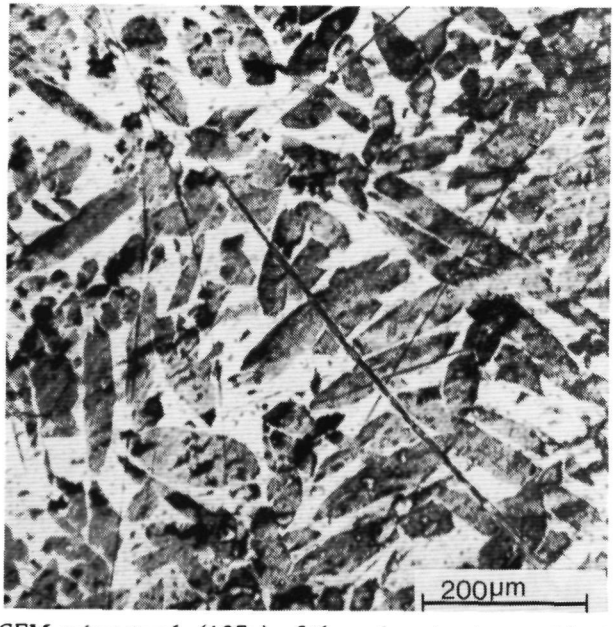


Fig. 7-16 A SEM micrograph (105x) of the microstructure evident on the buccal aspect of a Trindium crown (17 months).

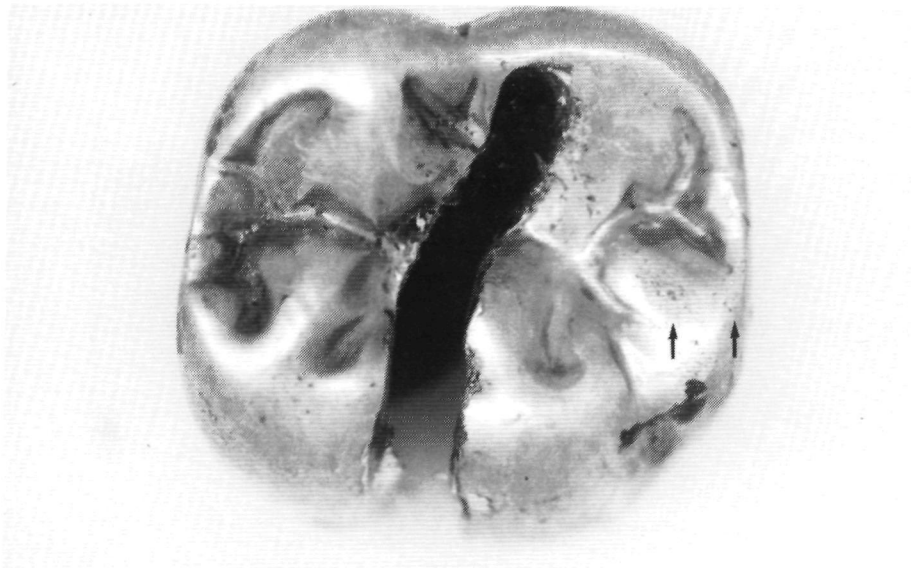


Fig. 7-17 An Auropall IV casting removed after 18 months in vivo, showing some wear on a relatively unchanged alloy surface.

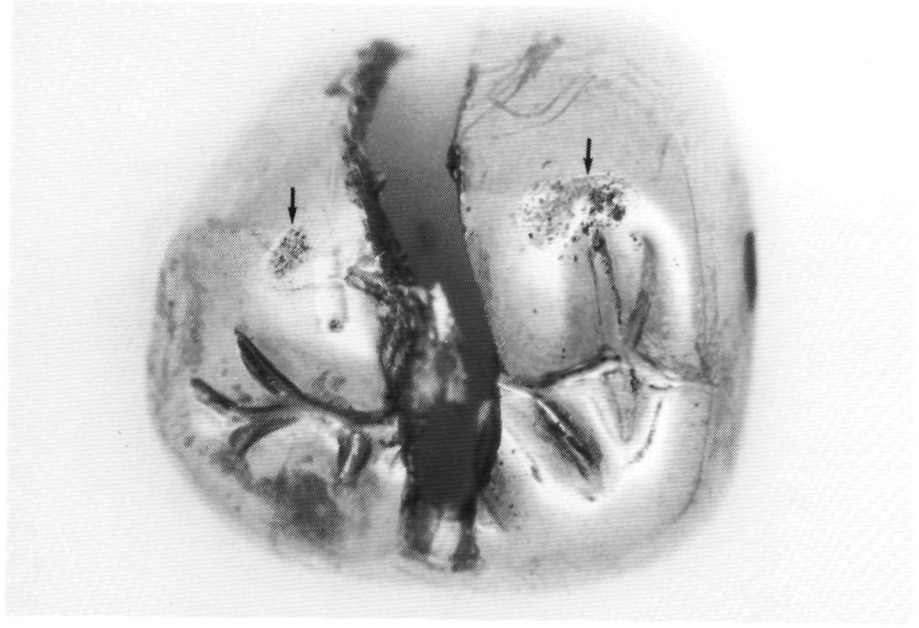


Fig. 7-18 Wear facets on a Palliag M crown after 21 months of clinical use.

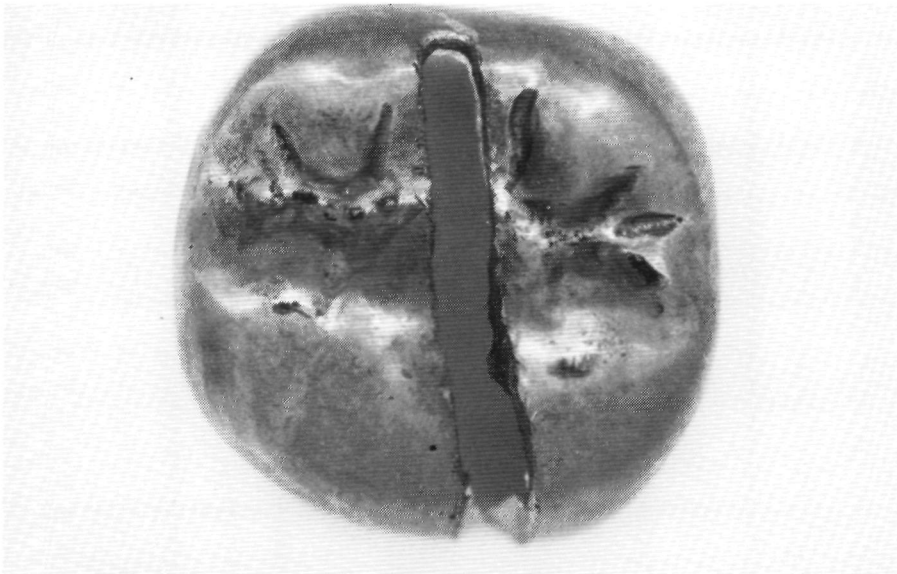


Fig. 7-19 The dull surface of a pure titanium crown after a clinical period of 15 months.

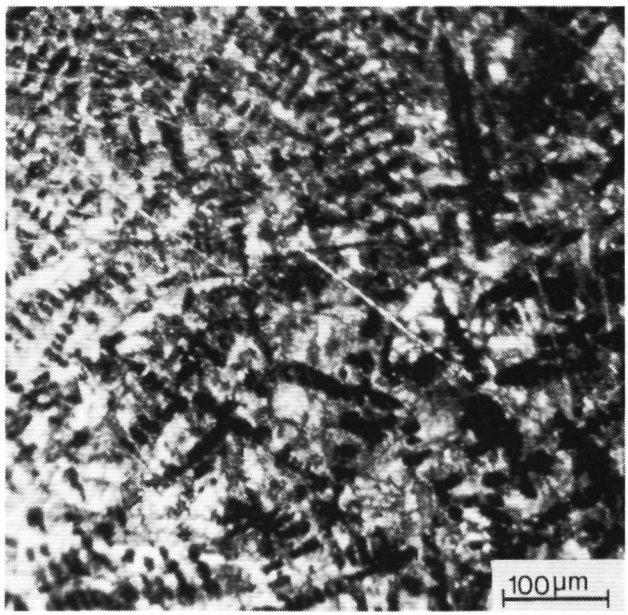


Fig. 7-20 A light-optical micrograph of the microstructure visible on a Ni-Cr-Be crown (Talladium) (80x) after 16 months of clinical use.

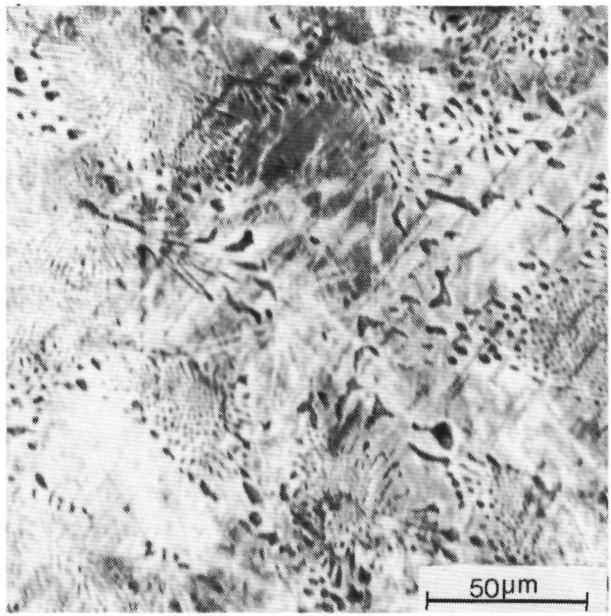


Fig. 7-21 Microstructure of the external crown surface of Talladium in the scanning electron microscope (420x) after 15 months in the oral environment. The NiBe phase is indicated with an arrow.

In some cases the proximal contact area showed a roughened surface. This finding was not consistent for any specific alloy or alloy and contacting material combination, though amalgam was often involved.
Under the stereo light microscope the other alloys did not reveal a microstructure.

7.3.3 Discussion

In this relatively short-term clinical study, a limited number (2 to 4) of cast restorations of each selected alloy was used. The results of such an experiment can only be considered as a comprehensive series of case reports with an emphasis on alloy changes possibly related to corrosion.
The possibility of removing the crowns after the trial period was important to enable the subsequent laboratory screening. The clinical findings, reported by the patients during the study, showed hardly any indication for oral galvanism related problems, despite of the different types of metallic restorations found in each patient. With the exception of a metallic taste sensation in one subject, none of te corrosion symptoms, as described by Wirz (1986) in non vital teeth, were defected. On theoretical grounds, use of only one type of metallic restoration in the mouth of a patient should be advocated, to prevent galvanic coupling effects. However, in everyday dental practice the use of a cast restoration in contact with

an amalgam restoration is frequently encountered. The same goes for the application of different casting alloys in one mouth. Based on the limited of this theoretically clear-cut problem, cannot be ascertained. A long-term clinical study on 15 low-gold casting alloys (Sturdevant *et al.*, 1987), where contact between different casting alloys was possible and amalgam-alloy contact was not excluded either, did not reveal any pain due to galvanic coupling, while other possible manifestations of oral galvanism were not mentioned either.

Clinical discoloration of a metallic restoration is visible to the patient as well as the dentist. The term is often used as a near-synonym for tarnish and thus commonly related to corrosion. In chapter 1, the problems with the definition of tarnish and its relation to corrosion have been dealt with. Both Letzel *et al.* (1983) and Sturdevant *et al.* (1987) indicated an important patient effect on the degree of clinical tarnishing of traditional and low-gold alloys. In our study, loss of luster of a casting alloy surface, a dulling effect due to plaque-like debris as well as discoloration films were found as aspects of colour change. Sturdevant *et al.* (1987) noticed that plaque accumulation on cast restorations was primarily located on the cervical third of a cast restoration. Although in their study tarnish clinically occurred in the same region, they could not establish a significant correlation between the presence of plaque and tarnish. The authors observed, however, that patients with a better oral hygiene had fewer tarnished restorations. In our results a relation between the plaque index value scored on the lingual surface and discoloration was established. This stresses the importance of patient-related alloy effects.

The variable aspects of tarnish, make it all the more difficult to assess distinct alloy changes. In case of a thin discoloration film, electron probe X-ray microanalysis may only give information about the relatively unchanged bulk alloy, while the excitation depth exceeds the discolored film. Moreover, quantification of the elements in case of a curved and (microscopically) irregular surface is very unreliable. In case of deposits of debris and plaque, the same quantitative measuring problems come up. Preliminary efforts of qualitative measuring of 'tarnish layers' only revealed the presence of S- and Cl-containing compounds. As an energy dispersive analysis with an electron microprobe cannot adequately discern elements with an atomic number < 11, carbon- and oxygen-containing compounds cannot be found. The analysis of extremely thin films on irregular surfaces goes far beyond the scope of this preliminary study and should be a topic for a separate extensive investigation.

Initial occlusal roughness of a cast restoration is caused primarily by mechanical wear. It may be reinforced by subsequently induced corrosion. Individual patient related factors as e.g. diet and (para)functional activities are of importance, though the hardness of an alloy may play some role too. An explicit corrosion activity is hard to distinguish. The roughening of proximal contact areas was scarce and inconsistent. It may be related to mechanical wear, due to physiological tooth mobility or aspects of corrosion. Galvanic coupling or the formation of a concentration cell in an area of easy plaque build-up may cause corrosive action. In case of distinct changes of free axial surfaces, a form of attack related to corrosion cannot be ruled out either.

Although no distinct microstructure could be distinguished under the stereo light microscope, the rough and dull aspect of the Mirafort 3L (yellow-low gold) clinical crowns might be indicative for a surface change possibly related to corrosion. This is hard to establish even with a scanning electron microscope, because the typical matrix-island structure of this alloy is also noticed on unetched flat polished alloy specimens (chapter 4).
Earlier experiences with the assessment of colour slides of crowns in the clinical situation made of a traditional ADA type III and a gold reduced (40 wt% Au) alloy (Mezger *et al.*, 1985) revealed however, that these axial surfaces may become dull and scratched irrespective of the choise of alloy, stressing a typical patient-related behaviour.
In case of Trindium, the aluminium-bronze alloy, a surface microstructure was evident at low magnifications (> 12) on all alloy surfaces, including the distinct attrition facets. Mueller and Barrie (1985, 1987) reported the clinical behaviour of some aluminum-bronze alloys with a copper content of 72-76 wt%. They found on crown surfaces a 'whitish-appearing precipitate', attributed to corrosion layers of sulphur- and chloride-containing copper compounds. The precipitate layer was absent on occlusal surfaces due to wear-related factors. Pre-placement finishing grooves on the alloy surface, still evident after the clinical trial period, led the authors to conclude a low corrosion activity under in vivo conditions. For Trindium, the same conclusion may probably not be made. In vivo exposure in our clinical trial produced a distinct microstructure, visible at a limited magnification (25x). It suggests a generalized surface corrosion activity (figs. 7-15 and 7-16). Metallographically polished flat samples of Trindium showed this microstructure under a light or scanning electron microscope only after an etching procedure. The results of the in vitro corrosion tests, discussed earlier in this chapter, are consistent with the indications of clinical corrosion activity.
Talladium, the Ni-Cr-Be alloy, kept its glossy clinical appearance and showed little attrition-related wear. However, also this alloy showed clinical indications of corrosion activity, evidenced by a microstructure, visible at a limited magnification (25x) under the light-microscope (fig. 7-20). Herø *et al.* (1987) used alloy discs of a Ni-Cr-Be alloy with a very similar chemical composition, embedded in removable acrylic dentures for clinical evaluation. They indicated an attack on the eutectic nickel-beryllium phase (fig. 7-21). Preliminary in vitro release data from a long-term submersion test in the artificial saliva with and without mucin (as used in chapter 3) substantiated this finding.
The Ni-Cr-Be type of alloy is recognized as suitable for the Maryland type of adhesive bridge (Thomson, 1982; Hill *et al.*, 1986), probably as it can be easily etched. Holste and Renk (1985) advocated in general non-precious multiphase alloys for adhesive bridgework, because selective etching of certain phases is easily accomplished. Easy etching may, however, be related to a dubious corrosion behaviour. Following this line of thought, Maryland bridges and periodontal etched-metal splints with their relatively large exposed alloy surface, might in the long run result in a potential health risk.
The other alloys did not show surface changes at magnification levels up to 50

times This does not necessarily indicate a total absence of corrosion activity in the clinical situation In this preliminary investigation, surface analysis has been limited to changes that are visible macroscopically and under the stereo light-microscope, because in this range distinct surface activity may be distinguished At higher magnification levels (> 400 times), using a scanning electron microscope, signs of a microstructure may become visible for the other alloys, e g some minor grain boundary etching A complicating factor is that at a large magnification level, the structure of some alloys is hard to distinguish on the clinically worn alloy surface or even on a perfectly flat etched alloy specimen Ewers (1986), using flat alloy specimens embedded in clinical acrylic removable dentures, could determine grain-boundary etching even for a gold-platinum-palladium ceramic alloy As this type of alloy has up to-now been considered to be a clinically proven standard for porcelain-fused-to metal crown and bridgework, this manifestation of corrosion activity may be considered to be of minor importance

Up to now, a number of assessment aspects for the crowns used in the clinical study have been discussed These criteria are related to corrosion phenomena possibly occurring in the mouth However, the variable, complex oral environment offers also alternative explanations for most of the alloy changes encountered Summarizing, table 7-5 shows the assessment aspects and evaluates their discriminative potential for the short-term corrosion behaviour of the casting alloys used

Table 7-5 Assessment aspects for the crowns used in the clinical trial and their discriminative potential for the short term corrosion behaviour of the alloys used

Assessment aspects	Discriminative potential
Patient complaints	−
Roughness occlusal surface	+
free axial surface	+
contact area	±
Microstructural surface change	+
Signs of oral galvanism	−
Periodontal breakdown	−
Plaque accumulation	−
Colour change of restoration	−

+ clear
± dubious
− absent

Based on distinct microstructural surface changes, indications of corrosion activity in the clinical situation are noticeable for Tindium, the aluminium-bronze alloy and Talladium, the Ni-Cr-Be alloy The obvious tendency of Mirafort 3L, the yellow

low-gold alloy, to loose its lustre, indicates surface changes, possibly related to corrosive action. Within the confines of this experiment, no firm indication of corrosion activity for the other alloys were found. The clinical behaviour of Talladium and Trindium was consistent with the in vitro corrosion tests. Both alloys are situated in the lower end of the corrosion spectrum, evidenced by high current densities in the area of oral interest in both electrolytes and high corrosion current densities. Mirafort 3L takes an inconspicuous place in the in vitro ranking. An exception must be made for its slightly higher and variable corrosion current density (I_{corr}), the singularly most important corrosion characteristic related to ion release.
A short-term clinical trial with a small number of castings per alloy, has limitations for a restoration type with an obvious longevity as a crown or a bridge. This type of experiment precludes a definite verdict on hazardous alloys, or the handing out of a 'safe and approved' sign for alloys, not displaying evident flaws. On the other hand, if signs of adverse alloy behaviour are found with relatively simple means in a short-term trial, one should be reluctant to use the alloys involved and look for more corrosion resistant ones. Only a large scale longitudinal research might lead to more absolute statements. Unfortunately, results of a long-term experiment tend to become obsolete in the rapidly changing casting alloy market.

7.4 Summary

The new alloy developments of the preceeding chapters 4 to 6 and two additional systems have been placed on the corrosion map.
The short-term clinical part of the study did not produce dramatic alloy or environmental changes related to corrosion in a period up to 22 months. However, the aluminium-bronze, the Ni-Cr-Be and to a lesser extent the yellow low-gold alloy, showed indications of corrosion-related surface changes. This would confirm tendencies from the in vitro behaviour. The possibilities to distinguish aspects of clinical corrosion from other environmental influences turned out to be limited in a short-term clinical set-up. The possibility to remove crowns for further laboratory screening was an useful aid.

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CHAPTER 8

Final conclusions and recommendations

The primary aim of this study was the assessment of the corrosion behaviour of dental castings alloys for crown and bridgework. Electrochemical techniques provide a relatively rapid and versatile means to screen different systems under identical laboratory conditions.

The corrosion profile derived is characterized by a combination of various parameters. A dental casting alloy should have a low corrosion current density under isolated conditions and low current densities at anodic overloading within the area of oral interest. It should preferably have a high ('noble') open circuit potential and no tendency to localized corrosion attack.

The corrosion data base presented in chapter 2 effectively provides ranges to illustrate 'high' and 'low' values for the spectrum of commercial alloys. However, exact boundaries of acceptability for clinical use cannot be formulated. For, apart from the quantity of ions released, their quality in terms of their biological implications in vivo, are not considered in an electrochemical study as these techniques register total charge transfer. Consequently, two systems with identical corrosion profiles are not necessarily equivalent from a biological standpoint.

The corrosion data base provided in chapter 2, allows for comparison of similar alloy systems and serves as a guideline for new alloy developments. The Pd-Ag and high-Pd alloys show a promising in vitro corrosion profile, while the yellow low-golds take an inconspicuous place in the spectrum.

Metallurgical investigation showed that the palladium-silver alloys are mainly single phase systems with an inhomogeneous character. The high-palladium and yellow low-gold alloys are more complex multiphase systems. This intricacy is reflected in the problems to fully identify and match the outcome of the X-ray diffraction and X-ray microanalysis. The influence of minor alloy additions on metallurgical aspects is noticeable for the Pd-containing alloy developments investigated.

However, within each of the subgroups, compositional and constitutional differences do not generally induce a significant difference in the in vitro corrosion behaviour, except for the corrosion current density of one yellow low-gold alloy.

The influence of mucin as a component of a commercial saliva substitute on the electrochemical corrosion testing of dental casting alloys, was limited to a pH dependent effect on the open circuit potential. The pH effects on mucin may simulate the effects of a biofilm on restorations. Mucin, added to this artificial saliva to obtain suitable rheological and wetting properties, has a certain buffer capacity. From the standpoint of corrosion testing its presence has turned out to be of minor importance.

The complexity of efforts to simulate the oral environment, stresses the importance of actual clinical research. The short-term clinical trial demonstrates, however, the limited possibilities the clinical evaluation armamentarium offers to distinguish aspects of oral corrosion from other oral influences. Additional in vitro screening of restorations removed from the mouth was necessary to reveal any significant corrosive action. This demonstrates the absence of gross manifestation of corrosion of the various casting alloys used in vivo, leading to possible mechanical failure. Nevertheless, distinct signs of surface corrosion attack leave the possibility of considerable ion release during the long lifespan of a cast restoration. Consequently, in case of the Ni-Cr-Be and the aluminium-bronze alloy, outliers in vivo and in vitro, one should consider alternative systems. Financial considerations should not be important, because there are alloys available, in the same market segment, which are more corrosion resistant.
One of the yellow low-gold alloys combines a mediocre in vitro corrosion behaviour with surface changes in vivo. Consequently, one would rank its corrosion behaviour below the other palladium-enriched alloy developments investigated in this study.
Titanium has good corrosion characteristics. Its widespread clinical use as a dental casting alloy is currently restricted, because of the sensitive and expensive laboratory techniques involved.
During the relatively short clinical trial period, electrogalvanism did not play a part in clinical behaviour. However, results from this patient group cannot be used to advocate the extensive use of dissimilar metallic restorations in the mouth.

Clinical experience with restorative materials is mainly gathered in the dental practice rather than in a research setting. This puts a heavy responsibility on the dentist, who chooses an alloy and should be aware of its chemical composition. The dental laboratory has to provide full information in case of change of alloy or technique used. Unless a major breakthrough in material science is expected, a frequent change is not desirable. Minor economic gain, related to a change within one alloy group, is not a base for selection. The cost of the alloys is in general a minor part of the end-price of a crown or bridge. The standards used for conventional crown and bridge alloys should also apply to adhesive bridgework.
It has been shown that post and core constructions require ultimate care in alloy selection. Modification or replacement of these restorations is hardly possible. Corrosion in the confined intra-radicular space may ultimately lead to root fracture. Galvanic coupling of totally different post and core metallic materials, including alloys with dubious passivating tendencies under unfavourable conditions, should be avoided.

Future research should include the identification of thin corrosive layers. Also an assessment of quantitative and qualitative aspects of ion release due to corrosive processes deserves more attention. In general, the biological activity and acceptability of restorative materials, their components and compounds remains an infinite field of investigation.

Summary

In *chapter 1*, the evolution of casting alloys used in crown and bridgework, along with some selected physical properties, were outlined. The large variety of alloy types, the considerable overlap of alloy characteristics between different alloy groups and the substantial differences found within each group, were stressed. Based on physical properties, a reasonable selection of casting alloys is possible. However, for the corrosion behaviour of these materials, prime subject of the study, this is not the case. Therefore, the main part of chapter 1 was dedicated to some general aspects of the corrosion process and the biological implications of the integration of metallic restorations in the oral environment. Finally the aims of the study were defined. They comprised the assessment of the in vitro corrosion behaviour of examples of the casting alloy spectrum with emphasis on three recent Pd-containing alloy developments, using established electrochemical techniques. Moreover, the influence of a mucin in a commercial saliva substitute for xerostomic patients on in vitro corrosion parameters of some casting alloys was investigated. Finally in a short-term clinical trial, aspects of clinical corrosion of casting alloys were introduced, to enable an in vivo and in vitro comparison.

Although test results of a number of casting alloys were available in the literature, a comparison was often not feasible because of the diversity of tests. Therefore, *chapter 2* served several purposes. The first part consisted of a general materials and methods section and presented the chemical composition of the alloys used (X-ray microanalysis). The second part of the chapter set out to create a corrosion map of dental casting alloys using established electrochemical techniques and two electrolytes. The difference between the 0.9% saline solution and the artificial saliva was reflected in the varying amount of the Cl^- ions and the presence of components with a certain buffer capacity e.g. phosphates. It gives some indication of individual patient-related corrosion effects.
Attention was given to the assessment of the precision of the measurement results upon replication. The meticulous sample polishing and other laboratory procedures did not preclude a substantial dispersion of measurements. Large differences in corrosion behaviour occurred within the base- metal alloy group.

Chapter 3 was dedicated to the influence of a mucin as a factor in the in vitro corrosion behaviour of 7 typical dental casting alloys. A commercial saliva substitute containing mucin to control its rheological and wetting properties and a control solution without this component, were used as electrolytes. Standard potentiodynamic techniques were employed to investigate the electrochemical behaviour in a region around the open circuit potential (OCP), as a function of oxygen concentration and pH.

The oral environment of xerostomic patients is particularly interesting, because it is partly defined artificially (by the saliva substitute). Consequently, laboratory conditions may closely mimic the in vivo situation.
The mucin component seemed to act as a cathodic inhibitor at pH = 6.7, but not at pH = 4.6, where the adsorbed film was evidently unstable. Another component of the saliva substitute (e.g. benzoate) acted as adsorption inhibitor.
The alloy effect on the corrosion behaviour found in chapter 2 and 3 may be trivial on the basis of the philosophy of the alloy selection. Still it is of practical value to stress that it is by far the most important factor. Therefore, in chapter 4 to 6, aspects of recent alloy developments were investigated. Not only the corrosion behaviour, but also the microstructure and lattice characteristics were screened for three types of palladium- containing alloys. The electrochemical techniques of chapter 2, X-ray diffraction, light microscopy and electron probe X-ray micro-analysis were used.

In *chapter 4* three members of a new family of low-gold (type IV) alloys were tested. This type of alloy is of particular interest, because the combination of a low-gold content and the absence of copper still results in a yellow coloured economy alloy. An ADA type III alloy was used as a control. The three low-gold alloys were very similar in chemical composition and showed a two phase matrix-island structure. The cubic 'island' phase, mainly consisting of the PdIn intermetallic compound, turned out to be responsible for the yellow colour.
In both electrolytes, the corrosion behaviour of the alloys investigated was similar until the upper, anodic boundary of the area of oral interest. There an increase of current density was observed, except for the control alloy. The corrosion current density (I_{corr}) for one low-gold alloy was significantly higher than for the other alloys tested.

In *chapter 5* the fairly recent palladium-silver porcelain-bonding alloys were investigated.
This alloy type was initially not so successful because of discoloration problems ('greening') at the metal-porcelain interface. Due to recent dedicated porcelain systems, a renewed interest in these alloys is noticeable.
The five alloys investigated, were mainly single phase systems, but they appeared to be inhomogeneous due to constitutional supercooling. Both indium-containing alloys showed signs of a minor second phase which could not be identified, probably due to its fine and dispersed character.
The corrosion behaviour of the palladium-silver alloys was quite similar irrespective of their microstructural and compositional differences. Corrosion resistance in the area of oral interest showed low current density values, while the corrosion current density (I_{corr}) showed low values for all alloys in both electrolytes. Under more extreme conditions of anodic overloading, the alloys were adversely affected by a high Cl^- content, resulting in a visible film.

The most recent palladium-based alloy development is formed by the high-Pd

alloys. *Chapter 6* comprises an analysis of nine examples of this type of porcelain-bonding alloy.
Based on X-ray diffraction measurements, the alloys, with one exception, were found to be complex multi-phase structures. Only after etching, the alloys showed a diverse microstructure under the electron microprobe. By means of quantitative energy dispersive X-ray micro-analysis or X-ray linescans, areas with distinct chemical compositions corresponding to the phases determined by X-ray diffraction, could not be found. Whether it concerned selective etching or fine and dispersed phases could not be substantiated.
Differences in microstructure and phase composition of the respective high-Pd alloys were not reflected in the corrosion resistance: their behaviour was equivalent and satisfactory in both electrolytes used.

In *chapter 7*, corrosion data of the new alloys investigated in this study were positioned in the corrosion spectrum of chapter 2. On the basis of the range of corrosion parameters of the alloy data base, two systems representing both sides of the scale and two representatives of an accepted older alternative alloy system were included for further clinical investigation. Furthermore, one non-commercial corrosion resistant system, titanium, was selected as well as a controversial commercial aluminium-bronze alloy with a bad in vitro prognosis.
For the in vivo part of the study a nickel-chrome-beryllium alloy, a class 1 type IV alloy, two silver-palladium alloys, titanium, aluminium-bronze as well as representatives of the new palladium-enriched alloy systems were included.
In total 28 crowns were made in the clinical trial. For each subject, different alloy types were inserted, allowing phenomena related to electrogalvanic coupling. The crowns were removed after 1 to 2 years to enable further laboratory screening.
The short-term clinical part of the study did not produce dramatic alloy or environmental changes related to corrosion in a period up to 22 months. However, the aluminium-bronze, the nickel-chrome-beryllium and to a lesser extent the yellow low-gold alloy, showed indications of corrosion-related surface changes. This would confirm tendencies from the in vitro behaviour. The possibilities to distinguish aspects of clinical corrosion from other environmental influences, turned out to be limited in a short-term clinical trial. The possibility of removing crowns for further laboratory screening turned out to be very useful in identifying surface changes.

In *chapter 8* it is concluded, that on the one hand the oral environment is actually needed to study corrosion effects, on the other hand the possibilities of the available clinical evaluation armamentarium is still limited.
The combination of in vitro and short-term in vivo corrosion research is no substitute for a large scale longitudinal clinical set-up. From the combined results gathered, the high-palladium and palladium-silver alloy systems seem promising, while the yellow low-gold alloy needs some modification yet.
Titanium has favourable corrosion characteristics, but its use as a casting alloy in restorative dentistry is restricted due to the difficult and expensive laboratory tech-

nique involved. The clinical study on crowns showed no or hardly tracable corrosive effects. This finding is in contrast with reported effects, which may result from the use of non-noble metals as posts and cores in non-vital teeth.
It is recommended that dental laboratories provide adequate information to the dentist with respect to the alloys used. Only this way the dentist can take full responsibility for his crown and bridgework.

Samenvatting

In *hoofdstuk 1* worden allereerst de ontwikkeling en enkele fysische eigenschappen van gietlegeringen voor kroon- en brugwerk behandeld. De grote verscheidenheid in legeringstypen, de overlapping van eigenschappen tussen de verschillende groepen en de aanzienlijke verschillen binnen iedere legeringsgroep krijgen de aandacht. Op grond van fysische/mechanische eigenschappen is een redelijke legeringskeuze te maken voor verschillende toepassingen. Voor wat betreft corrosie, het hoofdonderwerp van dit onderzoek, geldt dit echter niet. Daarom wordt vervolgens aandacht besteed aan het corrosieproces en de mogelijke biologische gevolgen bij klinische toepassing van gietlegeringen.
De doelstellingen voor het onderzoek kunnen als volgt worden samengevat:

- Het bestuderen van het in-vitro corrosiegedrag van een aantal representatieve gietlegeringen, met speciale aandacht voor recente palladium bevattende systemen.
- Het bepalen van de invloed van een mucine, als bestanddeel van een in de handel verkrijgbaar kunstspeeksel voor xerostomie-patiënten, op enkele corrosieparameters.
- Het onderzoeken van de klinische aspecten van corrosie en de relatie met het in-vitro corrosiegedrag.

Het laboratorium-onderzoek naar corrosie van gietlegeringen uit de bestaande literatuur, blijkt veelal niet vergelijkbaar in verband met verschillen in methodologie. Daarom werd in *hoofdstuk 2* naast de chemische samenstelling, het in-vitro corrosiegedrag van gietlegeringen uit het gehele spectrum bepaald met behulp van elektrochemische technieken. Deze groep van legeringen dient in het onderzoek als referentie. Als corrosievloeistoffen werden een relatief agressieve 0.9% NaCl oplossing en een min of meer representatief kunstspeeksel met een lager chloridegehalte en componenten met een bufferende werking, zoals fosfaten, gebruikt.
Naast de variatie van experimentele aard, waren de verschillen in corrosiegedrag binnen de groep van de niet-edele metalen opvallend.

In *hoofstuk 3* wordt de invloed van een mucine op het in-vitro corrosiegedrag van een aantal gietlegeringen onderzocht. De mucine-toevoeging aan kunstspeeksel dient ter verbetering van de bevochtiging en reologische eigenschappen. Voor de proeven werd een in de handel verkrijgbaar kunstspeeksel mét en zónder mucine gebruikt. Het elektrochemisch gedrag rond de rustpotentiaal werd bepaald als functie van de zuurstofconcentratie en de pH. Aangezien het mondmilieu van xerostomie-patiënten grotendeels wordt bepaald door het kunstspeeksel, lijken de klinische omstandigheden en die in het laboratorium op elkaar.

Uit de resultaten bleek, dat mucine bij een pH van 6,7 als cathodische inhibitor werkt en dat de aan het oppervlak gelegen laag bij een pH van 4,6 niet meer stabiel is. Een andere speekselcomponent, bijvoorbeeld het benzoaat, lijkt als adsorptie-inhibitor te werken. Zoals verwacht, bleek het effect van de legering zowel in hoofdstuk 2 als 3 het belangrijkst. Daarom komen in hoofdstuk 4 t/m 6 zowel de corrosie- als de metallurgische aspecten van drie nieuwe palladium-houdende legeringssystemen aan de orde. Gebruik werd gemaakt van elektrochemische technieken, röntgendiffractie en licht- en elektronenmicroscopie.

In *hoofdstuk 4* worden drie vertegenwoordigers van een type IV spaarlegering onderzocht. Ondanks een zeer laag goudgehalte en de afwezigheid van koper, hebben deze legeringen toch een goudkleur. De drie legeringen verschilden weinig in chemische samenstelling en bleken uit twee fasen te bestaan: een matrix met een vlakken-gecenterd rooster en een cubische eilandstructuur. De PdIn intermetallische verbinding, als voornaamste bestanddeel van de tweede fase, bleek de gele kleur van de legering te bepalen.
In beide corrosievloeistoffen was het corrosiegedrag van de drie laag-goudlegeringen en een ADA type III controle-legering binnen het klinisch relevante potentiaalgebied vergelijkbaar. Bij meer extreme anodische polarisatie nam de stroomdichtheid alleen voor de experimentele legeringen direct sterk toe. De corrosie-stroomdichtheid (I_{corr}) van één van de laag-goudlegeringen was significant hoger dan voor de andere legeringen.

In *hoofdstuk 5* komen de palladium-zilver opbaklegeringen aan de orde. Dit type opbaklegering is in opmars na het oplossen van de aanvankelijke verkleuringsproblemen aan het grensvlak van porselein en metaal. De onderzochte legeringen waren in het algemeen eenfasig, maar inhomogeen ten gevolge van onderkoeling. De indium-houdende legeringen bevatten wellicht een tweede fase, doch de fijne verdeling ervan maakte nadere identificatie onmogelijk.
Het corrosiegedrag van de palladium-zilver legeringen was vergelijkbaar, ongeacht verschillen in samenstelling en microstructuur. Binnen het klinisch relevante spanningsgebied waren de stroomdichtheden laag in beide corrosievloeistoffen. Bij meer extreme anodische polarisatie bleken de legeringen gevoelig voor de chloride-concentratie van de corrosievloeistof, getuige de zichtbare corrosielaag.

In *hoofdstuk 6* worden de hoog palladium opbaklegeringen behandeld. Röntgendiffractie-analyse liet complexe, meestal meerfasige legeringen zien. Evenals bij Pd-Ag legeringen was slechts door etsen van het legeringsoppervlak een microstructuur zichtbaar te maken onder de scanning- elektronenmicroscoop.
Noch kwantitatieve energie-dispersieve röntgen-microanalyse, noch 'lijnscans' konden echter verschillen in chemische samenstelling tussen de verschillende structuren/fasen aantonen. De corrosieweerstand van de acht onderzochte legeringen was in beide corrosievloeistoffen bevredigend.

In *hoofdstuk 7* worden de corrosiegegevens van de drie palladiumhoudende systemen in het corrosiespectrum van hoofdstuk 2 geplaatst Uit dit referentiekader werden twee uitersten op de schaal (een nikkel-chroom-beryllium en een klasse I type IV goudlegering), alsmede twee geaccepteerde alternatieve zilver-palladium legeringen voor nader klinisch onderzoek uitgezocht Voor dit doel werden bovendien het erkend' corrosiebestendige titaan en een controversiele, op de markt verkrijgbare, aluminium-koper legering geintroduceerd Van deze legeringen en vertegenwoordigers van de drie nieuwe palladiumhoudende systemen werden in totaal 28 kronen geplaatst bij tien patienten Contact tussen ongelijksoortige legeringen was toegestaan Na een periode van één tot twee jaar werden de kronen verwijderd voor nader laboratoriumonderzoek
Het klinische onderzoek leverde geen ernstige, aan corrosie gerelateerde veranderingen op Echter, zowel de Ni-Cr-Be, als de Al-Cu en de goudlegering uit hoofdstuk 4, toonden corrosieve veranderingen aan het legeringsoppervlak Dit komt overeen met verwachtingen op basis van het in-vitro onderzoek Echter, in het algemeen was de factor corrosie in klinisch onderzoek zeer moeilijk te onderscheiden van andere invloeden in de mond De mogelijkheid om kronen na verwijdering uit de mond te onderzoeken, is van groot belang

In *hoofdstuk 8* wordt geconcludeerd, dat corrosie-aspecten van gietlegeringen in de mond dienen te worden onderzocht, doch dat de klinische evaluatiemogelijkheden beperkt zijn De combinatie van een klinische korte-termijn studie en laboratoriumonderzoek vervangt geen grootschalige longitudinale klinische studie Echter, op basis van de gecombineerde resultaten lijken hoog-palladium- en palladium-zilverlegeringen veelbelovend Dit is in veel mindere mate het geval voor de recente laag-goudlegering
Titaan heeft goede corrosie-eigenschappen, doch is voor kroon- en brugwerk vanwege de dure en moeilijke laboratoriumtechniek nog maar beperkt toepasbaar
Het klinisch onderzoek liet slechts in zeer beperkte mate corrosieverschijnselen zien Dit staat in scherp contrast met de casuistische onderzoekservaringen bij niet-edele opbouwsystemen in avitale gebitselementen
Het verdient aanbeveling, dat tandtechnische laboratoria inzichtelijke informatie leveren over de gebruikte gietlegeringen, zodat de tandarts de verantwoordelijkheid voor aangebrachte gegoten restauraties bewust kan nemen

Appendix

1a Electron probe X-ray microanalysis

1b Measuring problems related to electron probe X-ray microanalysis

2 X-ray diffraction

3 Additional tables chapter 2

4 Dental laboratories and manufacturers participating in the investigation

Appendix 1a

Electron probe X-ray microanalysis

It is beyond the scope of the thesis to explain the electron microscrope and its applications in detail. The interested reader might be referred to text books on the subject (Reimer and Pfefferkorn, 1973; Hayat, 1974; Chandler, 1977). However, a brief introduction to electron probe X-ray microanalysis, as used in this study, must be included.
In the electron microprobe a focussed high energy electron beam strikes a surface and produces a number of signals, carrying structural and chemical information on the specimen, e.g. secondary and back-scattered electrons, characteristic X-rays as well as background X-rays. The low-energy secondary electrons may be detected, and the amplified detector signal may be used to obtain an image on a cathode ray tube screen, that can subsequently be recorded on photographs. For X-ray microanalysis the element-specific X-rays are used. These emerge when an inner shell electron of a specimen atom is removed by a beam electron with sufficient energy. The gap thus produced in the inner shell is filled with an electron from some other shell. The energy difference can be released as an X-ray photon and the amount is characteristic for the element and the energy jump concerned.
X-ray photons are collected by an energy-dispersive X-ray detector. After processing the signal, the result is an energy spectrum, which can be stored in a computer. To quantify the results, the background must be subtracted and the net special line intensities are compared to line intensities, derived from pure elemental standards. By well established arithmetic methods, element mass fractions can be calculated. For bulk specimens a special correction, the so called 'ZAF correction', is needed to obtain the actual element mass fractions.

References

Hayat, M.A. (1974): *Principles and Techniques of Scanning Electron Microscopy*, Vol. 1., 1st ed., New York: Van Nostrand Reinhold Co.

Chander, J.A. (1977): *X-ray Microanalysis in the Electron Microscope in Practical Methods in Electron Microscopy*, Vol. 5, part 2, 1st ed., A.M. Glauert, Ed., Amsterdam: North-Holland Publishing Co.

Reimer, L. and Pfefferkorn, G. (1973): *Raster Elektronenmikroskopie*, 1st ed., Berlin: Springer Verlag

Appendix 1b

Measuring problems related to electron probe X-ray microanalysis

The very low energy secondary electrons used to obtain an image, are generated in an extremely thin surface layer of the specimen. The contrast of the image mainly depends on topographical details (edges, surface irregularities) rather than atomic number differences. In our study the casting alloy specimens were examined in a polished condition. The surface structure was minimal and for most of the alloys etching was necessary to disclose details. When a specimen is struck by electrons, X-ray photons will emerge from a specimen volume having a depth and a certain area. According to the formula of Andersen and Hasler (1966) for Pd for example, the photons will be produced from a depth not exceeding 0.8 μm. Electron penetration depth into a specimen depends on the density of this specimen and the primary electron energy. With increasing atomic number the excitation area decreases. For the Camebax MB1 the diameter of the focussed electron beam, with an accelerating voltage of 20 kV at a total beam current of 10nA, is approximately 02 μm. When tiny structures are measured, the penetrating depth of the beam electrons might exceed the thickness of these structures. Thus the composition of the underlying matrix is measured rather than the structure intended.

An alloy specimen containing trace elements poses problems when the detection limit of the measuring system is reached. In a series of such measurements only in a part of the cases, a result statistically different from zero is found. Calculation of the mean and standard deviation for such elements becomes meaningless, because the average value for the total number does not deviate from 0. In the tables presented in this thesis, these elements are put into the category 'others': their presence cannot be excluded. However, an accurate determination is not possible.

A Si K-peak in a spectrum may be the result of detector Si dead layer fluorescence. An Al K-peak may result from stray electrons on X-rays hitting the Al specimen holder.

Reference

Andersen, C.E. and Hasler, M.F. (1966): Extension of Electron Microprobe Techniques to Biochemistry by the Use of Long Wavelength X-rays. In: *4th International Congress on X-ray Optics and Microanalysis*, R. Castaing, P.P. Deschamps and J. Philibert, Eds., Paris: Hermann, pp. 310-318.

Appendix 2

Experimental conditions of the X-ray diffraction experiments using an X-ray diffractometer with a stabilized generator (Philips, Eindhoven, the Netherlands).

Tube	Cu, 40 kV, 30 mA
Filter	Ni
Detector	Scintillation counter-probe
Divergence slit	1°
Scatter slit	1°
Receiving slit	0 2 mm
PHS window	150-300
Attenuation	2^4
Time constant	1 sec
Paper speed	20 mm/minute
Scanning speed	1°/minute
Range	4×10^3 cps

Appendix 3

In the tables 2-7 to 2-10 the electrochemical data of the class 3 to 0 alloys in the as cast condition are shown The tables 2-11 to 2-18 render the data of the porcelain-bonding alloys in the as cast (C) and simulated porcelain-fired (F) condition.

Table 2-7 Current densities in $\mu A/cm^2$ at several potentials (mV vs SCE) in 0 9% saline solution.

	Potential						
Alloy	−100	0	100	200	300	400	500
Degulor C	−0 1	0 3	0 8	1 1	0 6	0 7	0 9
Appolo IV	0 6	2 4	4 9	4 0	3 3	3 3	4 1
Protor 3	0 1	2 1	3 6	2 6	2 6	3 0	3 6
Oralit	−0 04	0 7	0 1	1 5	1 7	2 5	2 6
Minerva S	1 4	3 0	3 9	5 0	3 7	9 6	8 9
Medior 3	0 1	1 3	1 0	0 9	1 4	2 2	3 0
Pontallor 3	0 7	1 2	1 0	2 0	3 7	4 2	6 3
Mirafort 3	5 4	6 8	7 7	8 1	9 8	1 2	16
Auropall IV	0 2	0 5	0 7	1 6	2 6	3 1	748
Pallorag	0 3	1 4	1 4	3 6	10	1400	2180
Phobus Guss	0 9	2 0	82	43	46	694	1940
Palliag M	0 5	1 1	0 9	1 8	6 5	960	1940
Pallium 3	0 9	1 6	2 2	3 9	7 8	840	2010
WLW	8 8	8 9	13 4	22 5	68 5	984	2900

Table 2-8 Current densities in $\mu A/cm^2$ at several potentials (mV vs SCE) in artificial saliva

Alloy	Potential						
	−100	0	100	200	300	400	500
Degulor C	−0 1	0 4	1 2	1 4	1 0	1 1	1 6
Appolo IV	0 3	0 9	2 2	1 7	1 9	2 2	2 2
Protor 3	0 2	0 7	1 6	1 2	1 2	1 5	1 9
Oralit	−0 4	0 9	5 2	15	9 8	9 1	9 6
Minerva 3 S	1 2	1 4	1 8	2 7	2 6	2 7	2 7
Medior 3	0 1	0 8	1 3	0 9	1 3	1 9	2 0
Pontallor	0 6	1 2	10	8 3	9 4	10	12
Mirafort 3	2 8	4 5	5 1	4 9	6 6	8 1	10 2
Auropall IV	0 2	1 4	1 7	1 1	3 2	2 8	174
Pallorag 33	3 5	7 8	10	15	20	303	606
Phobus Guss	0 3	1 2	1 0	3 2	3 7	119	578
Palliag M	1 6	13	14	15	14	112	228
Pallium 3	1 2	4 4	4 1	5 2	8 7	133	468
WLW	1 5	2 4	2 6	4 5	7 3	43	106

Table 2-9 OCP (mV vs SCE), ZCP (mV vs SCE) and I_{corr} ($\mu A/cm^2$) in 0 9% saline solution

Alloy	OCP	ZCP	I_{corr}
Degulor C	+42	−87	0 02
Apollo IV	+8	−139	0 03
Protor 3	−8	−163	0 04
Oralit	+32	−95	0 08
Minerva S	0	−151	0 2
Medior 3	−21	−103	0 05
Pontallor 3	+3	−155	0 02
Mirafort 3	−18	−259	0 16
Auropall IV	−9	−171	0 06
Pallorag 33	−62	−111	0 09
Phobus Guss	+27	−139	0 2
Palliag M	−40	−163	0 04
Pallium 3	+3	−143	0 06
WLW	+3	−243	0 16

Table 2-10 OCP (mV vs SCE), ZCP (mV vs SCE) and I_{corr} ($\mu A/cm^2$) in artificial saliva.

Alloy	OCP	ZCP	I_{corr}
Degulor C	+70	−87	0 02
Apollo IV	+67	−131	0 09
Protor 3	+70	−131	0 04
Oralit	+69	−95	0 09
Minerva S	−14	−171	0 2
Medior 3	+23	−107	0 01
Pontallor	+70	−167	0 05
Mirafort 3	+8	−199	0 5
Auropall IV	−133	−123	0 06
Pallorag	−123	−159	0 04
Phobus Guss	+21	−123	0 03
Palliag M	+55	−159	0 13
Pallium 3	+65	−267	0 4
WLW	+61	−179	0 22

Table 2-11 Current densities in $\mu A/cm^2$ at several potentials (mV vs SCE) in 0 9% saline solution

Alloy		Potential −100	0	100	200	300	400	500
Degudent U	F	−0 1	1 3	1 8	2 2	2 2	2 1	2 3
A32	F	5 4	8 3	7 5	5 8	3 9	3 0	3 1
Orion WX	F	1 0	0 7	1 0	1 3	1 6	3 4	9 9
Deva M	F	−1 9	0 9	1 3	2 2	2 2	2 4	3 4
NP_2	F	1 6	1 5	1 5	1 6	1 9	2 4	3 2
Wiron 77	F	7 1	2 3	5 6	150	420	1200	3500
Wiron 88	F	1 4	1 7	2 7	17	110	180	140
Unibond	F	1 5	1 7	1 9	2 2	2 6	2 8	3 3
Talladium	F	2 3	39	1300	2000	3900	5800	7400
Vicomp	F	0 9	1 0	1 3	2 0	2 6	4 0	5 6

Table 2-12 Current desities in $\mu A/cm^2$ at several potentials (mV vs SCE) in artificial saliva

Alloy		Potential −100	0	100	200	300	400	500
Dugudent U	F	−1 6	0 5	0 9	1 0	0 9	0 9	1 2
A32	F	2 7	4 1	3 8	3 2	2 6	2 2	2 2
Orion WX	F	1 0	1 7	1 8	1 8	2 1	6 0	9 7
Deva M	F	0 8	2 7	2 9	2 6	2 2	2 8	3 2
NP_2	F	1 5	1 8	2 1	2 3	2 4	2 6	3 1
Wiron 77	F	1 3	1 6	2 6	8 5	16	77	220
Wiron 88	F	1 5	2 4	4 8	8 8	10 9	10 4	12 4
Unibond	F	1 1	1 3	1 6	1 7	1 8	2 2	2 8
Talladium	F	2 1	2 5	5 5	210	1800	4300	7200
Vicomp	F	1 7	1 9	1 9	1 9	2 0	2 3	3 2

Table 2-13 OCP (mV vs SCE), ZCP (mV vs SCE) and I_{corr} ($\mu A/cm^2$) in 0.9% saline solution.

Alloy		OCP	ZCP	I_{corr}
Degudent U	F	+120	−100	0 01
A32	F	+120	−170	0.05
Orion WX	F	+120	−70	0.04
Deva M	F	+160	−60	0.01
NP_2	F	−200	−320	0.08
Wiron 77	F	−270	−350	1.13
Wiron 88	F	−180	−250	0.65
Unibond	F	−170	−340	0.14
Talladium	F	−270	−370	2 23
Vicomp	F	−210	−370	0.09

Table 2-14 OCP (mV vs SCE), ZCP (mV vs SCE) and I_{corr} ($\mu A/cm^2$) in artificial saliva.

Alloy		OCP	ZCP	I_{corr}
Degudent U	F	+150	−50	0 03
A 32	F	+140	−160	0.22
Orion WX	F	+90	−140	0.04
Deva M	F	+110	−100	0 04
NP_2	F	−140	−380	0.43
Wiron 77	F	−70	−320	0.24
Wiron 88	F	−140	−400	0 09
Unibond	F	−150	−290	0 12
Talladium	F	−280	−311	0.37
Vicomp	F	−260	−370	0.05

Table 2-15 Current densities in $\mu A/cm^2$ at several potentials (mV vs SCE) in 0.9% saline solution.

Alloy		Potential −100	0	100	200	300	400	500
Degudent U	C	0.4	1.8	2.2	2.4	2.6	3 0	3.7
A32	C	0.5	2.2	2.4	2 8	3 2	4.7	5.3
Orion WX	C	−0.1	1 4	1.6	2.0	2 2	12	9.0
NP_2	C	1.7	3.2	5 2	9.7	20	48	100
Talladium	C	1.1	1.0	3900	20000	26000	40000	57000
Vicomp	C	1.2	1.2	1 3	1.2	1.5	2 0	3.2

Table 2-16 Current densities in $\mu A/cm^2$ at several potentials (mV vs SCE) in artificial saliva.

Alloy		Potential −100	0	100	200	300	400	500
Degudent U	C	−1.9	0.6	0.9	1 0	1.1	1 6	1.8
A32	C	1.0	1.3	1 3	1.2	1.1	1.6	3 0
Orion WX	C	−0.5	0.1	0.3	0 4	0 4	0.8	1.8
NP_2	C	1.7	1.9	2.0	2.0	2.0	2.2	2.5
Talladium	C	2.0	2.3	2.7	76	2100	4500	6500
Vicomp	C	2 1	2.2	2.3	2 4	2.5	2.8	3.9

Table 2-17 OCP (mV vs SCE), ZCP (mV vs SCE) and I_{corr} ($\mu A/cm^2$) in 0.9% saline solution.

Alloy		OCP	ZCP	I_{corr}
Degudent U	C	+110	−110	0 07
A32	C	+40	−110	0 13
Orion WX	C	+50	−100	0.11
NP_2	C	−190	−360	0 33
Talladium	C	−260	−430	0 22
Vicomp	C	−240	−400	0 13

Table 2-18 OCP (mV vs SCE), ZCP (mV vs SCE) and I_{corr} ($\mu A/cm^2$) in artificial saliva.

Alloy		OCP	ZCP	I_{corr}
Degudent U	C	+160	−60	0.07
A32	C	+40	−170	0 06
Orion WX	C	+120	−30	0.02
NP_2	C	−170	−340	0 32
Talladium	C	−270	−340	0 37
Vicomp	C	−240	−740	0.14

Appendix 4

Dental laboratories and manufacturers participating in the investigation.

Dental laboratory

Anto, Bergen op Zoom
Baarns TTL, Baarn
H. van Bemmel b.v., Leiden
Bosman b.v., Venlo
Broertjes b.v., Arnhem
Fr. v.d. Burg b.v., Groningen
Dental Lab. Fraba b.v., Bergen op Zoom
Geuzebroek b.v., Haarlem
P. v.d. Kamp b.v., Rotterdam
Heetveld, De Bilt
Dental Techniek Landa, Soesterberg
A.L.H. de Maat b.v., Heythuysen
Dental Ker. Lab. E.W.H. Mulder b.v., Wateringen
Novident, Nijmegen
Nijmeegs TTL, Nijmegen
Gebr. Prummel b.v., Groningen
Ker. Tandtechn. Lab. G..Scholten b.v., Tilburg
Tolmeyer Dental Lab. b.v., Arnhem
Dental lab. UTL (A. Sigterman), Utrecht
Ker. Dental Lab. Voit, Haarlem

Manufacturer

H. Drijfhout & Zn., Amsterdam
Elephant Edelmetaal b.v., Hoorn

Curriculum vitae

Peter Richard Mezger, geboren 16 november 1949 te Heerenveen.

1962-1968:	Gymnasium β opleiding aan Stedelijk Gymnasium te Utrecht.
1968-mei 1974:	Studie tandheelkunde aan de Rijksuniversiteit te Utrecht.
1974-okt 1975:	Dienstplichtig tandarts in West-Duitsland.
1975-mei 1978:	Wetenschappelijk medewerker van de afdeling Conserverende Tandheelkunde en Endodontie (hoofd: Prof. Dr. A.J. van Amerongen, resp. Prof. Dr. A.J.M. Plasschaert).
mei 1978-heden:	Wetenschappelijk medewerker van de afdeling Occlusie-opbouw (hoofd: Prof. Dr. A.F. Käyser).

Stellingen

behorend bij het proefschrift
CORROSION BEHAVIOUR OF DENTAL CASTING ALLOYS

P.R. MEZGER

1. Verschillen in fase-samenstelling en microstructuur van zowel hoog-palladium als Pd-Ag legeringen hebben niet noodzakelijkerwijs invloed op hun in-vitro corrosiegedrag.

Dit onderzoek

2. Mucine lijkt van ondergeschikt belang als factor bij in-vitro corrosie-onderzoek.

Dit onderzoek

3. Laboratorium-onderzoek van corrosieve eigenschappen van giet-legeringen is zowel vóór als na experimenteel klinische evaluatie nood-zakelijk.

Dit onderzoek

4. Goede etsbaarheid van een legering is een slecht selectie-criterium voor een gietlegering ten behoeve van een etsbrug.

5. Op grond van dit onderzoek dient goud in de zegswijze "Het is niet alles goud dat blinkt", vooralsnog niet vervangen te worden door palla-dium-indium en zeker niet door aluminium-brons.

6. De onwenselijkheid van gallium als het bestanddeel van NEM-legeringen is evenmin evident als de impliciete aanvaarding van dit element in Pd-Cu legeringen.

BEMA-Z richtlijnen (01-04-1986) voor legeringskeuze in West-Duitsland

7. De tandarts beseft in de praktijk onvoldoende, dat hij verantwoordelijk is voor de legeringkeuze van de door hem geplaatste gegoten restaura-ties.

8. Als gietlegeringen slechts na gecontroleerd klinisch longitudinaal onderzoek toegepast zouden mogen worden, waren er slechts enkele gietlegeringen op de markt.

9. Uitspraken over de frequentie en de dramatische gevolgen van corrosie bij gietlegeringen berusten voornamelijk op (spectaculaire) casuïstiek.

10. Het meten van potentiaalverschillen bij de patiënt is meer op mode dan op onderzoek gebaseerd.

11. "Dentristry is bad for teeth if you have a too active (restorative) dentist".

R. Elderton

"Many teeth are damaged needlessly by relying too much on preventive measures".

J. Mclean
BDA Annual conference, 1988

12. O vous les arracheurs de dents
Tous les cafards, les charlatans
Les prophètes
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Vrij naar "Oncle Archibald", G. Brassens

13. De bereikbaarheid van proefschriften wordt vergroot door de uitgave als supplement te koppelen aan een verwant wetenschappelijk tijdschrift.

14. Voor een onderzoeker is "Catch-22" (Joseph Heller) evenzeer van belang als een solide statistische kennis.

15. De wijze waarop de mens met het milieu omgaat, getuigt van een massale neiging tot zelfvernietiging.

Nijmegen, 26 januari 1989

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